# Electrochemical Industry

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## Electrochemical Industry

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J. W. RICHARDS, PH. D. .....*President.*

E. F. ROEBER, PH. D. .....*Editor.*

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### COMPLIMENTS OF THE SEASON:

We do not know how to start better the second volume of this journal than by presenting the compliments of the season to all our friends, and by extending our most sincere thanks to those who, by giving us their sturdy support, have made this journal, in a little more than a year, the representative exponent of electrochemical industries in America. On the title page of our first volume this journal is called "a monthly review of electrochemistry and electrometallurgy." From a friendly side we have heard a criticism to the effect that this journal should be, and has been, more than a mere review. While we have endeavored to give as concise and complete reviews as possible of what has been published either in the records of the Patent Office, or in other journals, yet the bulk of our editorial pages was devoted to the publication of original articles by authors who are building up the electrochemical industries. It is not often that a man who makes history cares to write it himself. But we are proud that in many cases we have overcome initial reluctance to publicity, and that the author's index of our first volume contains some of the best names in our industry and science. Some of them have been good enough to tell us that they support us, since they consider this journal to be their own journal; since they feel that this journal is conducted in the interest of the whole industry whose name it bears. The corps d'esprit of all the workers in various fields of electrochemistry and electrometallurgy has been the keynote of the success which this journal has met with so far; and it seems superfluous to add that we will not rest on our record, but will more than ever endeavor to increase the value of our pages to our readers. Then it may be that this journal, while being nothing but a technical newspaper, will become more than a review. In quite a number of cases we already know that information given in our columns has suggested to manufacturers valuable improvements, and has made people think of electrochemical methods who never thought of the same before. In this way, by the support of our friends, this journal may hope to do its share in aiding the development and progress of electrochemistry.

### PROGRESS OF ELECTROCHEMISTRY

While the year 1903 has not brought any surprisingly new developments in electrochemical industries, yet there has been great activity in all fields, and much conscientious and useful work has been done. When the electric furnace came into existence, entirely new industries sprang up like the calcium carbide and acetylene industry, and the manufacture of carborundum and artificial graphite. No such startling developments are to be recorded in the last year, perhaps, with the only exception of silixicon and the introduction of electric furnace methods in the metallurgy of special steels. The main

progress in the electric furnace line during the last year was devoted to the design of furnaces for special purposes. This development is fully described in the suggestive article by Mr. FitzGerald, published in this issue, while the progress in electrolytic processes and especially in the manufacture of aluminium, sodium, caustic soda, bleaching powder, chlorates and perchlorates, and in the whole electrolytic refining, and in the electroplating field is fully recorded in the able and interesting review by Dr. Richards, also published in this issue. In that part of electrometallurgy which relates to the production of metals direct from the ores, no industrial advances have been made during the past year, although much experimental work has been done in this line. The process of Mr. David H. Browne for the electrolytic separation of nickel and copper from the Sudbury ores, which was operated with good success for several years in Cleveland, and the operation of which ceased, for commercial reasons, after the consolidation of the different nickel interests in one trust, will again be put into operation after the completion of the new and extended works being in course of erection in Canada. The process of Mr. P. G. Salom for producing lead from the ores by cathodic reduction is not yet operated on a commercial scale, but an important advance has been made by the design of his new cell, which makes the operation continuous. In the metallurgy of gold the use of the electric current for the precipitation of gold from cyanide solutions is still largely confined to South Africa, although much experimental work is done in this field in this country.

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In the latest field of industrial electrochemistry, utilizing electric discharges through gases for producing chemical effects, the production of ozone from air and its use for sterilizing water is making headway in Europe, and the technical difficulties of the problem may be considered to have been solved. In view of the condition of the drinking water in many American cities, such processes should have a future in this country if the cost is not too high. The Bradley process for the fixation of atmospheric nitrogen is still in the stage of development. All the processes mentioned so far refer to the production of chemical effects by electrical means, while the reverse problem—the generation of electrical from chemical energy—covers the whole field of primary and secondary batteries. The most important development in this line is the appearance of the Edison storage battery on the market, on which we comment in another note. Concerning the old problem of electrochemists—the design of a carbon cell—this issue contains two articles. Prof. Lorenz' paper is especially valuable, on account of the lucid explanation of the thermodynamical principles to be considered in this problem, while Mr. Reed gives a very interesting critical analysis of the two latest attempts made by inventors in this field. The practice of estimating the growth and importance of applied electrochemistry by a review of the larger industries is, however, an underestimate of the services which that science is rendering. As Prof. Burgess points out in an article published in this issue, one should not neglect the numerous uses of electrochemical methods by which an economy of labor and materials is effected in various manufacturing industries. A striking example of such a saving is the method of electrolytic stripping of metals in the manufacture of bicycles described by Prof. Burgess. There can be no doubt that similar applications of electrochemical methods in other industries will greatly increase in future, as soon as the general manufacturer has learned that, as Dr. Richards puts it, electricity is such a kindly, such a manageable, such an all-potent agent, when its use is understood and mastered, that as a servant of mankind it may well be compared to the servant of Aladdin, the geni of the lamp.

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## EFFICIENCY CALCULATIONS

The usual method of calculating the energy efficiency of an electrochemical process is by comparing the energy required or given out, with the chemical energy calculated from the heat of reaction. In other words, we compare the energy required or produced by an electrochemical process, with the amount of heat which would be consumed or produced by the reaction if there was only an interchange of chemical energy and heat. We are, of course, at liberty to define the efficiency of a process to suit ourselves, but it may be interesting to point out that with the above definition we may occasionally arrive at very peculiar figures.

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To take the case of a galvanic battery, what we want to get from it is external work in form of electrical energy. It is usual to consider that we get this at the expense of chemical energy. Hence, the above definition that the efficiency is the ratio of the electrical energy given out by the battery, to the heat which would be produced if the chemical energy, lost in the battery, would be changed completely into heat. If we neglect for the present the inevitable losses, due to Joulean heat, etc., the efficiency of a battery may have very different values. As examples, we may take the different batteries discussed by Prof. Lorenz in the introduction of his paper on electricity direct from carbon, published in this issue. In case of the Daniell cell the efficiency, as above defined, is practically 100 per cent—because the chemical energy of the reaction in the Daniell cell is completely changed into electrical energy.

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In the zinc-silver cell, which is Prof. Lorenz' second example, the efficiency, as defined before, is 90.2 per cent, because this cell, while being discharged, tends to heat up, so that if the discharge is to go on at constant temperature—which is the first supposition of the application of thermochemical data—the cell must give off heat to the outside. In other words, the chemical energy lost in the cell is changed partly into electrical energy, and partly into heat; the electrical energy produced is, therefore, necessarily smaller than the chemical energy lost and the efficiency is below 100 per cent. In the third example of Prof. Lorenz—the lead-copper cell—the efficiency, as before defined, is 127 per cent. The reason is that the cell, while giving out current, tends to cool, so that in order to discharge it at constant temperature, we must supply heat from the outside to the cell and we have a change of both chemical energy and heat into electrical energy. The electrical energy produced is in this case necessarily greater than the chemical energy lost, and the efficiency, as defined above, is above 100 per cent. Even if we take into account the losses due to Joulean heat, etc., we may get, in a cell of this

type, an efficiency of over 100 per cent, as long as we define it by the ratio of electrical to chemical energy. But in practice we would have to heat the cell artificially, in order to keep its temperature constant and this heat would cost money. The efficiency is a practical item; we want to know what we put into a process, and what we get out of it. In the present case we do not only lose chemical energy, but have also to supply heat.

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Still more peculiar and more interesting is, however, the last example of Prof. Lorenz, in which he shows that an endothermic process may be used for the generation of electrical energy in a battery. An endothermic process has a negative heat of reaction, and in a cell of this type, while it is discharged at constant temperature, heat is supplied from the outside to the cell, and is partly changed into chemical energy, and partly into electrical energy. In this case it would be evidently foolish to try to use the term efficiency for the ratio of the electrical energy produced to the chemical energy produced.

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These examples indicate that it would be preferable to drop the above definition of the efficiency of an electrochemical system, and to define the efficiency rather as the ratio of the electrical energy which is produced to Helmholtz's "free energy" of the system. The latter quantity—not the heat of reaction—represents the maximum amount of external work which a reaction can perform. Hence, this definition of efficiency would give us exactly what we want to know: how much useful electrical energy we get in percents of the maximum amount of useful external work which it is possible to get under ideal conditions. The former definition of efficiency is essentially based on the assumption that Thomson's rule is correct, while the latter definition is based on the more exact Gibbs-Helmholtz equation. We know that at ordinary temperatures Thomson's rule is practically correct in the great majority of cases, but the higher we go up in the temperature the less exact it becomes, and the greater becomes the term of correction which distinguishes the Gibbs-Helmholtz equation from Thomson's rule. At the temperature of the electric furnace, calculations based on Thomson's rule might lead to absolutely wrong results, and for furnace calculations the efficiency based on the "free energy," instead of the heat reaction, seems very desirable. Of course, the trouble is that we have not such extended determinations of the free energy of a reaction, as we have of the heat of reaction. It seems a very promising field for research to determine systematically the free energy of all possible reactions in the same way as Thomson and Berthelot measured the heats of reaction, although it cannot be denied that the difficulties seem to be even greater than in the latter case.

## EDISON NICKEL-IRON BATTERY

Since the celebrated Edison nickel-iron battery has now made its somewhat belated appearance on the market, a brief summary of its distinguishing features may be of interest. From the description of the battery published in this issue, it appears that the capacity figure given by Dr. Kennelly in his original announcement of the battery in a paper read on May 21, 1901, and derived from tests with simple experimental cells—namely, 14 watt hours per pound—has exactly been reached again in the latest type of commercial cell, while the first commercial cell placed on the market had a somewhat smaller capacity. Besides its high watt-hour capacity per unit of weight, the capability of the Edison battery to stand very high rates of discharge or charge is of extreme importance. In this respect Prof. Hospitalier's comparative curves for the Edison battery and the lead accumulator, published in this issue, are highly interesting. With respect to durability the construction of the Edison battery is very assuring, being made, with the exception of the active mass, all of nickel-plated steel. The use of a stiff and easily worked metal for the support plates and the packing of the active mass in perforated pockets with stiff covers should prevent the battery from being deteriorated to the same degree as the lead accumulator. In the mechanical perfection of his battery Mr. Edison's inventive ingenuity and mechanical skill have certainly achieved one of their greatest triumphs. While concerning durability and strength the use in practice has, of course, the last word to speak, yet the results so far obtained look very promising, and it cannot be denied that in the mechanical construction of his cell Mr. Edison has endeavored to render it as fool-proof as possible. Of course an oxygen lift cell can be more easily perfected in this respect than the lead accumulator, which, as someone once said, will always need more or less nursing during use.

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Considered from an electrochemical point of view, the main feature which distinguishes the Edison battery from the lead cell is to be found in the role which the electrolyte plays in the reaction. In the lead accumulator the electrolyte is really an active reagent, because it undergoes change during charge and discharge, sulphuric acid being consumed during discharge, and produced during charge. A certain number of ampere hours requires necessarily a certain quantity of sulphuric acid. On the other hand, in the oxygen-lift cell the electrolyte, as a whole, is not changed. The change of the dilution of the electrolyte in the pores of both plates of the lead accumulator during discharge, is the principal reason for the drop of voltage during discharge; this is especially important at high discharge rates, when the acid is quickly diluted in the pores of both plates with a resulting rapid drop of voltage, as though the whole solution had been diluted to the same degree. On the other hand, it seems probable that in the Edison cell for average discharge rates the slight gradual drop is mainly due to an increase of internal resistance. There is a tendency of local concentration increasing in the one plate and decreasing in the other, but the drop of e. m. f. due to these local concentration changes is small, in accordance with the theory. In the curves of the Edison cell such a drop of voltage clearly manifests itself only at the highest discharge rate; this indicates that the active masses are sufficiently porous for average discharge rates. While the position of the lead accumulator seems secure for electric station work—at present estimated at about 75 per cent of the total storage battery output—the features of the Edison battery, pointed out above, should make it especially suitable for automobile purposes, and now that Mr. Edison's battery has finally been placed on the market, we may hope that this will mark the beginning of a new era in electric automobilism.

## AMERICAN ELECTROCHEMICAL SOCIETY.

The next general meeting of the American Electrochemical Society will be held in Washington, D. C., on April 7, 8, 9.

The following gentlemen will be elected members at the January meeting of the Board of Directors: J. T. McNaier, Philadelphia, Pa.; Kenneth B. Quiman, Somerset, W., Cape Colony; G. L. Townsend, Washington, D. C.; Henry M. Loomis, Niagara Falls, N. Y.; Orion Brooks, San Francisco, Cal.; Charles A. Marie, Paris, France; P. L. T. Heroult, La Praz, France; G. Orth, Nancy, France; Fred. L. Shinn, Madison, Wis.; A. Gandillon, Geneve, Switzerland; O. Solvay, Brussels, Belgium; Louis A. Herdt, Montreal, Canada; William Stanley, Great Barrington, Mass.; Edwin J. Prindle, Washington, D. C.; H. M. Fernberger, Niagara Falls, N. Y.; Frederick Conlin, Bethlehem, Pa.; William L. Dudley, Nashville, Tenn.; Henry P. Talbot, Boston, Mass.; Raymond Outwater, Washington, D. C.; Darragh de Lancey, Great Barrington, Mass; Ernest R. Barrows, Brandt, Pa.

## METAL STATISTICS.

The latest volume of the Comparative Statistics of Lead, Copper, Spelter, Tin, Silver, Nickel, Aluminium and Quicksilver has recently been issued by the Metallgesellschaft and Metallurgische Gesellschaft A-G. of Frankfort-on-the-Main, Germany. We are obliged to Dr. Franz Meyer, New York City, for a copy of this volume. It contains a great number of statistical tables on the production and consumption of the metals mentioned, in the different years between 1893 and 1902, with some notes on the development during 1902.

The world's production of *lead* in 1902 is given as 863,000 tons, and has, therefore, increased by 24,000 tons, while in 1901, it only increased about 6,000 tons. This increase in the production is all the more remarkable, as four mines in the Broken-Hill district in Australia had to stop working in consequence of the low price of the metal, which caused a falling off of the production to the extent of 25,000 tons of lead.

According to calculations which comprise the produce of the smelting works, the world's production of *copper* amounted to 533,000 tons in 1902 (while H. R. Merton & Co., of London, give it as 550,000 tons). This is an increase of about 3 per cent over the preceding year, which is entirely due to the United States of America, where the production from home material has risen from 271,000 to 363,000 tons.

The world's production of *spelter*, which already showed the considerable increase of 29,000 tons = 6 per cent in 1901, has again increased, in 1902, by further 38,000 tons = about 7½ per cent, thus reaching the figure of 545,000 tons. The increase is chiefly due to the United States, Great Britain and Upper Silesia (Germany).

The production of *tin* amounted to 88,300 tons in 1902. In the United States, in consequence of the favorable position of the tin-plate industry, the consumption rose by more than 10,000 tons to 39,300 tons, thus amounting to 45 per cent of the world's production.

The world's production of *nickel* in 1902 is given as 8,335 tons, of which 4,715 were produced in the United States and Canada.

The production of aluminium is given as 8,111,000 kg. in 1902 (against 7,810,000 in 1901, 1,426,760 in 1895 and 333,307 in 1891). The variation of the price of one kilogram of aluminium is seen from the following data: $250 in 1855, $17.50 in 1886, $6.90 in 1890, $1.00 in 1894, $0.50 to $0.62 in 1900 to 1902.

## SECOND MEETING OF THE FARADAY SOCIETY.

The second ordinary meeting of the Faraday Society was held on December 8, in the library of the Institution of Electrical Engineers, in London. Prof. A. K. Huntington presided.

Dr. Lehfeldt gave a short résumé of his paper on "The Total and Free Energy of the Lead Accumulator," which was already noticed in Electrochemical Industry, vol. I., page 413. The most convenient form in which to express the concentration of acid in the accumulator, for the present purpose, is by the molecular function (Z) of $H_2SO_4$. The heat of the reaction (in equivalents)

$$\tfrac{1}{2}Pb + \tfrac{1}{2}PbO_2 + H_2SO_4 = PbSO_4 + H_2O$$

may then be put in the form—

$$h - \frac{dQ}{dZ}$$

where $h$ is the heat of reaction between the pure materials (in absence of water) and Q is the heat of formation of the mixture $Z.H_2SO_4$ $(1 - Z)H_2O$. Numerical values of this are calculated from the experimental data already in existence for the range $Z = 0$ to $Z = 0.25$, and the results shown by a curve. The free energy can be put in a similar form. A curve is drawn for it, based on e. m. f. measurements, and the latter are compared with the vapor pressures (p) of dilute $H_2SO_4$ by the relation which must exist between these quantities, according to the principles of thermodynamics.

Dr. Ogg sent in a short note, in which he tested the numbers derived from Thomsen's formula, and compared them with those derived from Pickering's experiments. The former all lie below the latter, probably because the Thomsen formula does not absolutely represent the heat of mixture of $H_2SO_4$ and $H_2O$.

Dr. Lowry made some remarks on the basis of the sulphate theory, observing that sulphating is usually looked upon as a "disease."

Dr. Lehfeldt, in his reply, said that the adoption of the sulphate theory is justified by the fact that measurements of the changes of weight in the Pb, $PbO_2$, $PbSO_4$ and $H_2SO_4$ agree tolerably closely with those deduced from the equation given in the paper. Sulphating, however, in the sense used by practical men is not the same as the formation of sulphate during discharge, where only a film is allowed to form, and is immediately broke down by the current during charge.

Mr. J. A. Sutherland then read a paper entitled "Bitumen in Insulating Compositions" (Part I.). The author points out that little or no reliable data have been published, as to the use of bitumen for electrical purposes. The chief source of bitumen is Trinidad Lake, where there is estimated to be a quantity of nine million tons, which appears to be renewed to the extent of 20,000 tons annually. Upwards of 150,000 tons are exported yearly. Bitumen is also found in Venezuela, California, and on the shores of the Dead Sea; it occurs in some limestone (asphalt) as an impregnation, about 10 to 15 per cent being present, but it does not pay to extract it from this source. Its physical and chemical properties and constitution, which are fully dealt with in the paper, prove it to be infinitely superior to gas or coal tar for insulation and durability. Care should be exercised in refining; the temperature should be regulated, or the results will be injurious, both for paving and electrical purposes. It is used in cable insulation, and very extensively for joint boxes and troughs for "solid laid" cables. No specification is, however, in use, and the object of this paper is to invite discussion and the views of electrical engineers to assist the author in the completion of his experiments, and to enable him to draw up a satisfactory definition of bitumen, so that users may secure the best results from its valuable non-hygroscopic and insulating qualities.

Gaster referred to Roumanian sources af asphalt. He has succeeded in freeing pitch from its carbon, which can then be used for arc carbons and electrodes, but the pitch still retains too much oxygen to be a satisfactory substitute for bitumen.

Dr. Steinhart strongly supported the author in his remarks regarding the desirability of arriving at some standard tests for bitumen. Physical, as well as chemical and electrical tests are required. E. Kilburn Scott said that some firms declare that refined pitch is as satisfactory as bitumen.

## THE PRESENT STATUS OF THE ELECTROCHEMICAL INDUSTRIES.

BY JOSEPH W. RICHARDS, PH. D.

Almost without exception, the present is a time of growth and expansion in this industry. Most of us can remember without trying very hard, the time when electrochemistry, as an industry, included silver and gold plating, and the electro-refining of copper. It is hard to realize that the first electrolytic copper refining plant in this country is not twenty years old, and yet now we are producing eighty-five per cent of all the electrically refined copper made in the world. The last twenty years have been practically years of the creation of industries, no one knew or could even guess what the next monthly journal would record as a new factor in industrial electrochemistry.

Untiring experiment, unwearying endeavor, undaunted application, and many unsuccessful enterprises, have marked the path and the development of these twenty years. But, one by one, the commercially successful schemes have gained a footing, little by little they have gotten onto firmer ground, and now there exists a large grove of flourishing industries, in the midst of a healthy growth of promising saplings, which may soon grow into big oaks themselves. Competent observers, not themselves electrochemists, have noticed this development, and have published their testimony to the fact that this branch of industry is the most rapidly advancing one in the catalogue of the applied sciences.

Such a condition attracts not only attention, but also enlists co-operation. Our young men ask their friends what is the best thing for them to go into, and an increasing number are referred to electrochemistry. Nothing succeeds like success, the saying goes, and the successful industry attracts capitalists, promoters, business men, technologists of every description, and also attracts the interested and enlists the assistance of scientists in general.

The present status is, all things considered, a healthy and a promising one. None of the industries seems to have reached its limit of progress or improvement, none is at a standstill, and many are continuing the inroads they are making in established non-electric methods.

The production of the alkaline metals cheaply by electrolysis has superseded all other methods, and the field of use for these metals is rapidly extending. Within a year the production of metallic sodium at Niagara Falls has been doubled. The largest use is probably for making sodium cyanide for the cyanide process of treating gold ores, and since the latter is extending with considerable energy, there are bright prospects for the extension of the sodium industry. Renewed efforts are being made to use sodium as a reducing agent in metallurgy, and some simple devices may render this use practicable.

The production of alkaline salts from the cheap alkaline minerals is also progressing apace. In the manufacture of caustic soda and bleaching powder from common salt, the electrochemist has come into direct competition with one of the best established and technically the best-developed of the chemical industries. The war has been strenuous, but the non-electric industry is now practically at the mercy of the electrolytic processes. It is estimated that in England alone forty million dollars of invested capital has been concerned in this defeat of an established industry. The victors, however, have begun quarreling over the spoils, the rival electrochemical plants have cut the prices of their products down to such a degree that it would appear at present that the only hope for the industry is a mutual understanding by which competition may be regulated within reasonable bounds, and the electrochemists thus get the reward of their labors. In this strife, it appears to the writer that while the aqueous mercury processes have so far been the most successful, that they have probably reached nearer to their possible ultimate perfection than the diaphragm or the fused-bath processes, and that the latter, being susceptible of greater improvements, will, in the future, hold their own quite as well, if not better than before, in competition with the mercury processes. The alkaline chlorate industry is already conquered for the electrolytic methods, the non-electric processes have fled the field. It is, therefore, with them, a question of supply, demand or proper production to make a profitable business. The manufacture of other alkaline salts, such as bi-chromates, permanganates, etc., is already being undertaken, mostly by the chlorate manufacturers, who are looking for new worlds to conquer.

The manufacture of electrolytic bleach is increasing in extent and importance. This branch of electrochemical science is particularly useful to the extension of the industry in that the multiplication of small electrochemical plants in numerous localities serves to excite a widespread interest in electrochemical methods, gives facilities for experiment to many would-be electrochemists, and thus paves the way for further advances, while the saving over non-electric bleaching preaches a loud sermon to the capitalist.

The electric plating industries are our pioneer electrochemical industries, and while we may not say that they are increasing in importance, like the other sister industries, yet there is no doubt that the activity and spirit of research, and particularly the spirit of scientific exactness which is ruling in other electrochemical arts is reacting very favorably towards the obliteration of old rule-of-thumb traditions and mediæval practices, and the substitution therefor of accurate measurement and control. When all the conditions are known, and quantitatively controlled, they can always be produced with exactness, and such terms as luck, good-fortune or mystery go out of the back-door. Abundant signs of this awakening have been shown this year in the plating industries; some of our most prominent electrochemists have given their best attention to the subject, many timely articles have appeared in the journals and scientific transactions, and the plating business of the future is very evidently going to pass into the control of the wide-awake men who keep fully abreast of the scientific advance of the times.

The copper refining industry is advancing splendidly. One particular characteristic is the different avenues of advance in different parts of the country. One large plant in the East goes back to the almost discredited series system, claiming that, as they have improved it, it is better than the parallel system. Another huge plant out West uses the high current density of 40 amps. per square foot, while its neighbors, forty miles away, not blessed with such cheap power or such pure anodes, keep pegging away at 12 amps. One plant removes its cathodes every four days and melts them down, another every two days and strips them, while a third, knowing exactly what his competitors are doing, keeps his in a month. These variations in practice are of the opposite significance to what they would have been ten pears ago; then they would have meant that each stuck to his own method largely from inertia; now they mean that each has convinced himself, by trying all the other schemes, that his is the best under the conditions in which he is working. The industry has been described by Mr. Ulke, in his book on Electrolytic Copper Refining. Prof. Bancroft has contributed an article which, in spite of what his critics have said, is a most valuable contribution to the science of electrolytic refining of copper, and the records of the other scientific journals and of the patent office testify to the continual advance of this industry, all branches of which are feeling the stimulus towards higher efficiency and reduction of costs.

The electrolytic refining of lead bullion has all at once flashed up among us, not as a proposed method, but as a good-sized plant already in commercial operation. The event is something akin to the birth of a baby ten years old. How often we have admired the pluck of Dr. Keith, trying thirty years ago to solve the same problem, and how often the question has been since attempted, but now Mr. Betts, with his

almost unknown electrolyte, fluo-silicate of lead, shows us how easy the thing is to accomplish when you once know how. A recent newspaper item stated that 60,000 ounces of silver from his plant at Trail, B. C., had just reached the San Francisco assay office, and that the refining plant was in process of being multiplied by three. The results of the working of the plant have been reported in a most scientific manner and with most commendable frankness, to the scientific journals, thus increasing the debt which electrochemists owe Mr. Betts and the admiration which they feel for him and his work. When experience has been gained at this plant, there is no reason why this method of refining should not spread among the lead refineries like measles in a kindergarten. Wherever coal is dear and power cheap, there is the opportunity for the electrolytic method to get a foothold. I know of no more encouraging chapter in the history of electrochemistry, for the perusal of our coming workers, than to study the rise and development of Mr. Betts' process. It is fascinating, and an epitome of what may happen in scores of other industries when the educated and capable electrochemist gets fairly and actively to work at them.

One of the oldest electrochemists in America has under his charge one of the newest electrochemical refining processes. Dr. Tuttle, of the Philadelphia Mint, has described very clearly how he is operating the Wohlwill process of refining gold, and the information is very welcome. With the successful working at Philadelphia as a start, we may expect other plants at Government and private establishments to get into operation, and thus another electrochemical industry to take its place in the galaxy of recent achievements. Every successful new process, when properly and completely described, is a sermon to the electrochemist on how difficulties have been overcome, and gives him training in meeting the novel difficulties of his own special problems. Thus, when gold chloride alone is used as solution, only a fraction of the gold is dissolved from the anode which the current should dissolve, but by acidulating strongly with hydrochloric acid, the normal amount is dissolved. Betts found something similar with lead and hydrofluoric acid. The knowledge of these facts helps every electrochemist and electro-plater, and has in no wise injured the givers. May we have a healthy growth of this spirit of mutual helpfulness among American electrochemists; it is really this which is sending us ahead of the rest of the world.

The electric de-tinning of tin scrap has finally found a lodgement in the United States, and it is to be hoped that we have seen the last of that humiliating spectacle of shipments of tin scrap from Baltimore and New York to Hamburg. Like the tin-plate industry, once here we believe it is here to stay, and the Staten Island plant will be an object lesson in how to treat such material which will probably soon lead to the similar treatment of all kinds of metallic scrap which needs un-plating.

The two thousand words which the editor asked me to write on my topic are already written, and, as nearly as I can estimate, five thousand more would be necessary to do equal justice to all the electrochemical industries as yet unmentioned. Therefore, we must be brief.

The electric manufacture of pig iron is a scientific possibility but commercially impossible: the electric manufacture of steel, by any of half a dozen proposed ways, is not only practical but practicable, and already in use for manufacturing a high-grade tool-steel, where power is cheap and fuel dear. It is the writer's belief that the days of crucible steel are numbered; that is, the maker of electric steel may still call his product "crucible steel," to help sell it, perhaps, to those who have all their lives asked for crucible steel, but when the electric steel furnaces are perfected a little more, the costly crucible, with its 60-pound charge, will be a back-number. This branch is distinctly in a transition state, but developing rapidly, and a few years will see a fixed electric-steel-furnace practice replacing most of our crucible steel plants.

Aluminium has come through a tempestuous year in some respects, the pending litigation and uncertainty of its outcome unsettling both the producers and consumers. The faith of the manufacturers in the future demand for this latest of commercial metals is shown by the increase of the capacity of the lower Niagara works by 3,000 hp, which together with the starting of operations at Massena gives this company something like 22,000 hp now in operation, or double the sum of all its European competitors. The uses for the metal are growing apace, and the writer abates not one jot of his conviction that the next generation will see aluminium one of the most common metals in every day use, and selling at a price which will make it practically the cheapest metal next to iron. This year has seen substantial advances toward that goal.

The electric manufacture of calcium carbide, carborundum, manufactured graphite, artificial emery, phosphorus, electrolytic vanillin and carbon-bisulphide, have all flourished during the year. Those of the electric reduction of lead ore, production of nitric acid from atmospheric air, manufacture of barium compounds and several others have been more or less sucessful, and all promise well for early development into successful commercial enterprises.

Besides the full-grown and the developing, there are also the prospective processes and industries, whose consideration would alone make a long chapter. Electrochemists have only scratched the surface of the possibilities of applied electrochemistry. Like the philosopher, they have been picking up pebbles on the sea shore, and a whole ocean of possibilities lies before them. Electricity is such a kindly, such a manageable, such an all-potent agent, when its use is understood and mastered, that as a servant of mankind it may well be compared to the servant of Alladin, the geni of the lamp. Each passing year is destined to record an increasing catalogue of its beneficial services, and each year will increase the interest and the fascination of the subject to live electrochemists.

## ELECTRIC FURNACE INDUSTRIES IN 1903.

By F. A. J. FitzGerald

A review of industries using the electric furnace, for the past year, does not show any remarkably novel developments; but there has nevertheless been great activity in this field, more especially in the designing of new furnaces. The majority of these are still in the experimental stage, but may eventually become of commercial importance, while many others obviously will not survive. Anything approaching a complete review of the work done in electric furnaces during the past year would be altogether impracticable in a limited space, and therefore it will only be possible to glance at a few examples which are instructive as indicating the probable direction of future developments.

One of the most interesting branches of electric furnace work in Europe is that of the manufacture of ferro-alloys and steel. It is curious to note here that, notwithstanding the fact that the United States is to-day the largest producer of iron and steel, large quantities of ferro-alloys are still imported from abroad.

The work of Keller, of Keller, Leleux & Co., at Livet, France, is of particular interest, and has been very fully described by Mr. Keller* in his paper before the *Iron and Steel Institute*. His company is at present using about 2800 kw in the manufacture of ferro-alloys, special grades of steel and copper. In the Keller furnace the hearth is not used as one of the electrodes, the current passing from one electrode, through the charge to the other electrode. By using two or more pairs of electrodes it is possible to make the working of the furnace continuous, as one pair of electrodes may be changed at a time. Another important feature of this design is that by making an arc between the electrode carbons and the charge, the contamination of the metal by carbon is said to be avoided.

*Electrochemical Industry, 1903, pages 420 and 162.

The Héroult process for the manufacture of steel has some features in common with Keller's furnace, two electrode carbons being used and the current passing through the bath from one to the other. In the furnaces designed by Stassano and Chavarria-Contardo, however, the principle is different, for in them the material under treatment is heated by radiation from an arc.

In Kjellin's process a totally different principle is made use of, the material treated forming the secondary of a transformer. This process is interesting, and is said to be very satisfactory; but it has not yet been worked on a sufficiently large scale to demonstrate its commercial value.

The Kjellin furnace is of the resistance type, and from its principle avoids altogether the use of carbon electrodes and the consequent introduction of carbon from that source into the metal.

Gin in his latest process, described elsewhere in this issue of ELECTROCHEMICAL INDUSTRY, uses a furnace in the form of a long, narrow channel, the terminals consisting of large reservoirs, where the metal is kept in the solid state, thus furnishing the furnace terminals.

Girod is designing crucible furnaces in which the crucible is surrounded by a resistance material through which the current passes. His company, La Société Anonyme Electrométallurgique, has works, or is about to start works at various places, Albertville and Ugine (Savoie), and at Courtepin (Switzerland). In the latter place 4000 kilowatts will be employed. A great variety of products are manufactured: ferro-alloys of silicon, molybdenum, tungsten, chromium, vanadium, etc.

In Europe more attention seems to have been devoted to the application of the electric furnace to the metallurgy of iron than to any other process, since the days of the calcium carbide boom. Some work has been done on its use in the manufacture of glass, but this difficult problem does not as yet seem to have been solved commercially.

Some interest was excited by a resistance furnace designed by Dorsemagen, for the simultaneous production of carborundum and metallic zinc from silicious zinc ores; but it is quite safe to say that the furnace, as described in the patent, could not possibly be worked commercially.

Turning, now, to this country, it will be noted that, as in Europe, much work has been done in the application of electric furnaces to processes in which relatively low temperatures are required. In a furnace patented by Acheson, the purpose is to heat materials between definite limits of temperature. In most of the electric furnace processes of earlier days the object was to raise a mass of material to a very high temperature, and the question of temperature regulation was not of the first importance. In Acheson's work on carborundum manufacture, he found that above a certain temperature his product was decomposed, and hence he designed a new form of electric furnace, in which the temperature could be regulated. However, in the carborundum furnace the permissible range of temperature is great, or in other words, the difference between the temperatures of formation and decomposition of carborundum is considerable. In the process of the manufacture of carborundum an amorphous substance of a greenish color is first formed, and the temperature limits in this case lie very close to one another. To manufacture a substance of this description, the furnace must be so designed that very accurate temperature regulation is obtained. To accomplish this result, Acheson built his furnace with several cores, which carry the current, and are thus maintained at the upper limit of temperatures, while the cores are so placed, relatively to one another, that the points of lowest temperature between them are at or above the lower limit.

Acheson uses this furnace for the production of a series of silicon-carbon-oxygen compounds which he has named "siloxicon." The material has a very refractory nature, and is said, in certain experiments made on a large scale, to have proved satisfactory; which encourages the hope that it will prove of value in other places. So far, about 130,000 pounds of the material have been manufactured.

In a process recently patented by F. J. Tone, is found another example of a furnace constructed in such a way that careful temperature adjustment can be obtained. This process is for the reduction of oxides whose temperature of reduction lies close to the temperature of volatilization of the reduced substance. The furnace is of the resistance type, the heating body being composed of a vertical column of carbon blocks piled together and forming electrical connection between the upper and lower terminals. It is said that the results obtained with this furnace in the production of silicon are very satisfactory.

A further example of the use of electrical furnaces for relatively low temperatures is found in Hall's process for the baking of carbon electrodes, and his process of removing silica from coke. The unbaked electrodes are arranged about a central core of conducting material, and a current passed through the core, which raises it to a high temperature. The heat thus developed bakes the electrodes at a "temperature higher than that ordinarily obtained in gas furnaces." While it is difficult to understand how a uniform baking of the carbon electrodes can be obtained by the method as described in the patent specifications, it is interesting as an example of the application of the electric furnace to temperatures very little higher than those obtained in fuel furnaces.

The manufacturers of calcium carbide, the largest users of electric furnaces, have not apparently made any radical changes in their furnace practice. The Carborundum Company expects to use 5000 hp in electrical furnaces next year, and will have a 2000-hp furnace, without doubt the largest resistance furnace that has ever been constructed.

It would be impossible to review even briefly the numerous patents that have been taken out for various types of electric furnaces, but it may be noted that a study of recent developments in this direction reveals the growing interest in furnaces of the resistance type.

As regards the future of the electrical furnace, two important considerations must be kept in view. Before the advent of the electrical furnace, the maximum temperature attainable in industrial processes was somewhere between 1500° and 2000° C.; but now a maximum temperature between 3500° and 4000° C. may be obtained. Thus the manufacturer now has at his disposal a great range of temperatures hitherto unattainable.

The second point to be considered is that in transferring heat from one body to another by conduction, the rate of transference varies directly as the difference of the temperatures of the bodies. In certain processes, where fuel is used as the source of heat, the temperature which it is desired to reach differs but little from the temperature of the source of heat. Here the expenditure of energy is necessarily very great, on account of the long time required to obtain the temperature desired at the end of the run.

Both these considerations are now claiming the attention of inventors. In the earlier days of electric furnaces their use was devoted exclusively to such processes as the manufacture of carborundum, calcium carbide, graphite, etc., where very high temperatures unattainable by other means are required; but now the electric furnace is being used for processes requiring temperatures that lie in the region between the temperatures of burning fuel and the electric arc. Such processes are illustrated by Tone's method of manufacturing silicon, Acheson's manufacture of "siloxicon," and the furnaces of Keller, Girod, Harmet, Héroult and others for the production of certain ferro-alloys.

But in addition to this we find the electric furnace also applied in processes where the necessary temperatures are not above those attainable by other means. Keller, Héroult, Gin, Stassano, Chavarria-Contardo, Kjellin, in Europe, and Ruth-

enburg in this country propose to use electric heat for the production of iron and steel; Hall uses the electric furnace for baking electrodes at temperatures that cannot easily be obtained in gas furnaces; and various other inventors, too numerous to mention in detail, are experimenting with the electric furnace at temperatures that represent the limit that can be reached by other means.

It seems probable that before long there will be new industries undertaken to develop processes requiring those temperatures which lie between the temperatures attainable by ordinary means, and that of the electric arc. In certain processes where very high temperatures that cannot be obtained by means of burning fuel are not required, it may be expected that the electric furnace will find a place, on account of the great economical advantages in the use of electricity, where these lie in the possibility of generating the heat at the place where it must be used, or in the high temperatures that may be given to the heating mass.

Finally, it does not seem unreasonable to look for the use of the electric furnace as an auxiliary to furnaces of other kinds, where a point is reached at which the attainment of high temperatures can be most economically reached by electrical methods.

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## ELECTROLYTIC STRIPPING OF METALS.

By Prof. Charles F. Burgess.

A number of years ago, when the manufacture of bicycles was in its most prosperous stage, an important department in each factory was that devoted to filing, where the thin layer of brass on the surface of the frames was removed by a corps of workmen stationed at benches around the room. The trouble and expense incurred in maintaining this department induced the manufacturers to seek a relief, which was found through the agency of the electric current. As a result, the filing room was changed to an electrolytic stripping room, which was free from labor troubles, and in which the work proceeded more quickly, cheaply and satisfactorily than had been possible previously.

The common practice of estimating the growth in importance of applied electrochemistry by a statement of the values of the products manufactured is an underestimate of the service which that science is rendering. It neglects many uses to which the electric current may be put to effect an economy of labor and materials in various manufacturing industries. A striking example of such a saving is that to which reference has just been made in connection with the manufacture of bicycles.

In assembling bicycle frames the method of brazing the joints which formerly was most commonly used, consisted in dipping them in a bath of molten brass, thereby leaving upon a portion of the surface a thin film of brass which it was necessary to remove in order to apply a suitably adherent coating of enamel. The method by which this was first effected consisted in filing the exterior brass. This was uneconomical, as it entailed a cost for labor of about twenty-five cents for each frame. Moreover the frame was weakened as a result of removing a portion of the steel. With the thin steel tubing which was used, the removal of even a slight amount of the material meant a considerable loss in strength, and slight carelessness or lack of skill on the part of the workman became a matter of no small moment.

An idea that then naturally suggested itself was to remove this brass through the dissolving action of certain chemicals. Among materials which were tried, but which produced only partially satisfactory results, were potassium cyanide and sodium or potassium bichromate solutions. The slowness of the action and the large consumption of chemicals made necessary prevented this from becoming a practical solution of the problem, and the next attempt was the use of the electric current to aid in the solvent action. This produced satisfactory results, as stated previously.

Although this process has been in use for a number of years, it has received little or no attention in technical publications, so that a somewhat detailed description may be of interest. The removal of the brass from the iron is effected in the manner known by the plater as the "electrolytic stripping process," in which the current is made to corrode the surface material without injuring the underlying metal. Inasmuch as there are only a few grams of superfluous brass on each frame, and somewhat evenly distributed, it would appear that the application of a suitable stripping solution might be a simple matter, but difficulties were encountered in finding practical electrolytes. These arose from the fact that when a number of different metals are in contact, and are used as the anode, the tendency is for the most electropositive metals to corrode the more readily. In the case under consideration, we have a combination of zinc,

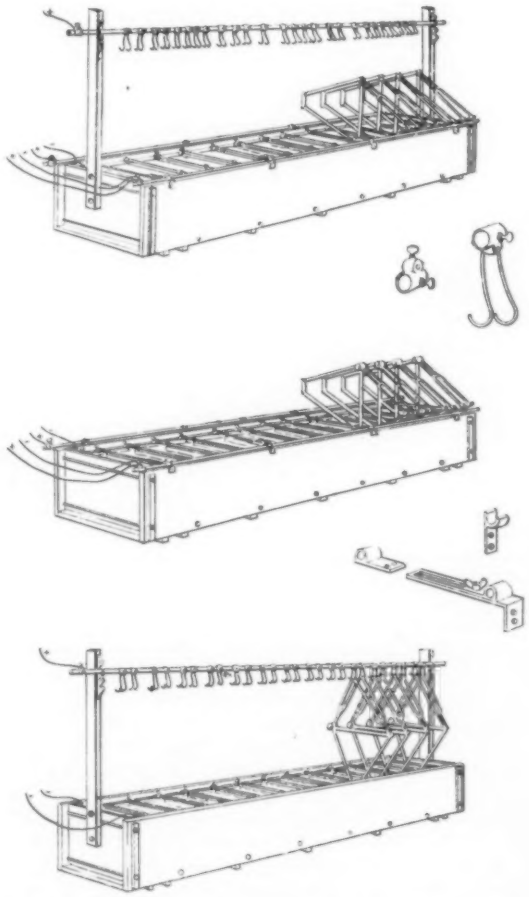

FIG. 1.—TANKS AND FITTINGS FOR STRIPPING BRAZED BICYCLE JOINTS.

iron and copper whose positions in the electrochemical series are in the order given, and the zinc is the metal that is the most readily soluble of the three. The dissolution of a small amount of zinc from the brass leaves a copper surface, which is electronegative to the iron. This brings about a tendency for the iron to be corroded before the copper. In an experimental investigation of this problem, undertaken in the laboratory of Applied Electrochemistry of the University of Wisconsin by Mr. M. C. Beebe and the writer, a large number of electrolytes were tried, but none would cause a corrosion of the brass, while leaving the iron uncorroded. It was found, however, that by taking advantage of the so-called passive state of iron, a peculiar property which that metal assumes in certain solu-

tions, that the relative positions of the iron and the copper in the electrochemical series could be reversed and the corrosion of the iron thus prevented. This can be accomplished by using a nitrate solution, sodium nitrate on account of its cheapness and electrical conductivity being the most practical material at hand. In a paper presented at the September meeting of the American Electrochemical Society*, the results of experiments dealing with this passive condition of iron were described.

It was found that upon placing the iron and brass as the anode in a sodium nitrate solution and causing the current to flow toward an iron cathode the zinc and copper could be completely removed, leaving the iron smooth and bright. When a sodium nitrate solution, freshly prepared by dissolving sodium nitrate crystals in water, was used, it was found that it required some minutes for the iron to become passive, but after the solution had been in use for some time, the iron would become passive almost instantly upon placing it as the anode in the solution. A study of this phenomenon revealed the fact that during the passage of the current a small amount of sodium nitrite was produced at the cathode which subsequently diffused throughout the solution, and that it is the presence of this nitrite which aids in the production of the passive state of the iron. It was also noted that after the tanks had been in operation for several days the iron would again lose its passive condition and become corroded almost as readily as if the solution were a chloride or a sulphate. The cause of this was found to be due to a change in the electrolyte, whereby the electrolyte was made quite alkaline with a considerable liberation of ammonia. In keeping the solution in an efficient condition it was therefore necessary that this alkalinity be prevented. This can be done by the occasional addition of a small amount of free nitric acid.

The tanks used for this treatment of bicycle frames, as constructed and installed by the Hanson & VanWinkle Company, are illustrated in the accompanying sketches. Each tank has a capacity suitable for the class of work to be treated therein, the tanks for the front forks being shallower than for the other joints on account of the various forms to be treated. It is desirable to immerse the joints into the solution only far enough to expose the brass, and a few inches should be allowed below the lower part of the anode to allow for the accumulation of sediment. The tanks are usually constructed of carefully selected two-inch pine, and are bolted together to prevent leakage. The method of suspension is considerably different from that used in the ordinary plating tank. The cathodes are placed cross-wise in the tanks and at sufficient distances apart to permit the insertion of a piece of brazed work between them, allowing a distance of one or two inches between the anode and the cathode. The cathode usually consists of sheet iron or steel plates of about No. 14 gauge, which are permanently connected by brazed copper connection to the negative bars of the tank. The anode connections are usually effected by the simple weight of the work upon the strips or bars constituting the positive terminal. When the weight of the work is not sufficient to insure satisfactory contact, an increase in pressure may be produced as shown in the illustration. Each special class of work requires a particular construction of the terminals in order that the work may be handled most economically.

In cases where the entire object must be suspended in the solution, the suspension hooks should be made of iron or steel, copper or other materials being easily corroded by the action of the solution. The electrolyte consists usually of a solution of sodium nitrate of a purity of 98 or 99 per cent dissolved in soft water. One pound of this material to a gallon of water will give a good workable solution. Five degrees B′ is a density usually employed, and the hydrometer serves as a satisfactory indicator for maintaining the solution at its proper density. In using the hydrometer, however, it should be remembered that the indication when the solution contains a large amount of sediment in agitation will be too high and a test should, therefore, be made in a clear solution. The following table gives some data on the solutions of sodium nitrate at different densities.

$NaNO_3$

| % $NaNo_3$ | s. g. | °B′ | resis. pr. c. c. |
|---|---|---|---|
| 5 | 1.0327 | 5 | 23 ohms |
| 10 | 1,0681 | 9 | 12.8 " |
| 20 | 1.1435 | 18 | 7.66 " |
| 30 | 1.2278 | 31 | 6.22 " |

From this table it will be seen that densities higher than those usually employed will give a solution of lower resistance, but such advantage is not sufficient to warrant the use of a more concentrated solution, which has the disadvantage of not allowing the ready precipitation of the copper and zinc hydroxides which are formed, thus interfering with the proper action of the solution. An economy of material is also effected by using the dilute solutions, inasmuch as when the sediment is removed from the tank only a small amount of the sodium nitrate is wasted.

It is sometimes advisable to add a very small percentage of sodium nitrite to the solution when it is first prepared, as this will insure the immediate desired action of the solution upon the passage of the current. The addition of this, however, is not necessary, for after the tank has been in operation for some time some sodium nitrite is formed at the cathode.

The solution operates most satisfactorily when in a neutral condition. During operation there is a tendency for it to become alkaline, as will be explained later, and this alkalinity is shown by the red litmus paper becoming blue when dipped into it or by the odor of ammonia which may escape if the alkalinity is allowed to proceed to a considerable degree. For satisfactory working, this alkalinity should be neutralized by the occasional addition of nitric acid which should be added in small quantities each day. If the alkalinity be allowed to proceed too far and neutralized by a considerable quantity of nitric acid at any one time, it may cause a vigorous evolution of nitrous fumes and this should be avoided so far as possible, as the corrosive fumes are harmful not only to the workmen, but to any metal work exposed to them. By adding the acid in small quantities and properly diluted from day to day, the liberation of nitrous fumes can be entirely prevented.

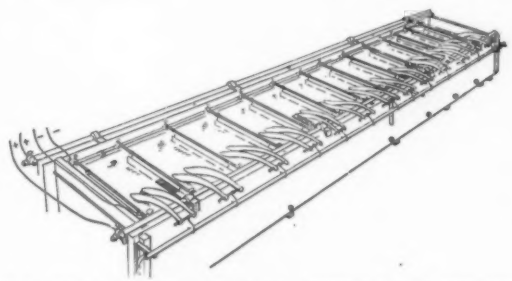

FIG. 2.—TANK SHOWING SPECIAL FITTINGS FOR STRIPPING FRONT FORKS.

The proper amount of acid may be determined by the litmus paper test. If the acid be added in a slight excess no damage will be done to the solution, as it merely results in dissolving some of the precipitate, and the presence of such excess of acid is made evident by a deposition of copper upon the iron cathodes.

Some users of this process compound the electrolyte by neutralizing sodium carbonate or sodium hydroxide with nitric acid, but the cost of the solution thus prepared is much greater than when prepared directly from the sodium nitrate crystals. The solution should be comparatively free from sodium chloride or sulphates, and, inasmuch as certain grades of sodium nitrate on the market contain a considerable percentage of these

*Electrochemical Industry, 1903, page 483.

materials, care should be used in obtaining sodium nitrate of a suitable degree of purity. Otherwise, the solution will cause a dangerous corrosion of the iron.

It may be observed that after the solution has been used continually for a number of hours it heats up, and when thus heated the results obtained are not so satisfactory as at lower temperatures. To reduce this heating, either the tanks and the volume of the solution should made larger or the current density decreased. By an examination of the anodes from time to time, it may be determined whether the process is working satisfactorily. This is shown when the brass is removed rapidly, leaving upon the surface a brownish layer which may be rubbed off readily, exposing the bright yellow brass. When there is a thick greenish precipitate adhering to the brass it shows that the solution has become alkaline and the appearance of a brownish precipitate and a brown scum accumulating upon the surface of the electrolyte indicates that the alkalinity has proceeded so far as to cause corrosion and pitting of the iron.

The brass, after it is removed from the anode, is precipitated in the solution as a flocculent greenish-blue precipitate which remains suspended for some time, but gradually settles to the bottom. While the process is in operation, a portion of this material rises to the surface in the form of a scum, and after some experience and observation the appearance of this surface will give an indication of the condition of the solution.

The precipitate may finally accumulate to such a degree as to interfere with the action of the electrolyte, and it is then necessary to remove it. This may be done by drawing off the solution from the bottom of the tank, which carries with it a great deal of precipitate. By allowing this to stand for some time in barrels the clear solution may be drawn from the top and replaced in the tanks. Another method for cleaning out the tanks consists in allowing the solution to settle over night and then siphoning the clear liquid above the sediment. This sediment, which is a mixture of zinc and copper hydroxide changing upon standing to the oxide, represents a waste in the process, for, although it contains metals having considerable value, a method of recovering them cheaply has not yet been worked out.

The current density used in the process may have a value of from five to fifteen amperes per square foot, and with such current densities, and with a solution in the best condition the layer of brass may be removed in from five minutes to forty-five minutes, this depending upon the thickness and uniformity of the coating. If there are lumps of brass of some thickness it may take even longer time to remove it completely, but under such circumstances it is usually more economical to remove these thicker portions by subsequent filing.

The pressure required for this work is between three and five volts, though if the leads from the dynamo are not of sufficient size it may be necessary to have the dynamo pressure of a higher value. Where a considerable amount of work is to be treated in this process, low pressure dynamos of a large current capacity are required. In fact, the introduction of this method of stripping has created a demand for the largest size low-plating dynamos which have been constructed so far. A machine having a compound winding is especially advantageous in this work, as the tanks will operate at the same rate, whether fully loaded or only partially so. Another requirement is that the dynamo should have a sufficient copper brush-bearing surface to prevent excessive heating from the large volume of current required. The conductors leading from the dynamo to the tanks should be of the highest conductivity copper, and of a sufficient size to prevent an excessive drop in them when the tanks are drawing the maximum amount of current. While many plants have conductors of too small a size, it is possible to err on the other side and have conductors which entail unwarranted expense in their installation. A large-sized conductor will allow the use of a lower dynamo pressure, thereby saving energy, but this saving in energy may not be sufficient to counterbalance the greater outlay for copper.

Success in working this process depends upon keeping the solution at the right concentration and chemical composition, removing the articles at the proper time, and applying a suitable current density. The better the brazing has been done, the more satisfactory is the stripping process. If the work is allowed to remain in the tanks too long the current may cause corrosion of some of the brass within the joints, thereby weakening them, but if the joints have been properly fitted and brazed such weakening may be made negligible. A limitation of this process is that brass can be removed only with difficulty from cast iron, such iron not assuming the passive condition, but this is not true of malleable castings, and in wrought iron and steel no trouble from corrosion need be experienced.

After removing the work from the tanks, the pieces are brushed with bristle brushes and water to remove the loosely adhering material, and are then dipped in hot water and allowed to dry in the air, after which no subsequent corrosion will occur unless they are exposed to moisture.

In the manufacture of automobile parts, and in many other instances where iron is subjected to the brazing process this electrolytic stripping method may find useful application.

Silver, copper, tin, zinc, lead, cadmium and their various

FIG. 3.—SHEET IRON SURFACE FROM WHICH TIN HAS BEEN REMOVED ELECTROLYTICALLY IN A SODIUM NITRATE SOLUTION.

alloys can be removed from iron in this way, and this points out various other applications of the process. It offers a convenient and rapid method for removing silver from plated articles of iron, which are to be resilvered, and also for removing the silver from suspension rods, hooks, and baskets used in silver plating, thus not only recovering the suspension devices themselves, but the silver as well. The silver separates as a sediment in the solution, and by proper heating or chemical treatment may be recovered in useful form. Suspension devices used in copper cyanide solutions may be similarly treated.

Files which have been used upon brass, copper, lead or other soft metal, and have become clogged, may be quickly and effectively cleaned by suspending them as the anode in a sodium nitrate solution.

The layer of tin on tinned iron may be removed completely in a few minutes in the same manner without dissolving any of the iron. This operation may furnish a possible solution of that problem which has received considerable attention of late, the recovery of tin and iron from scrap tin. The question of

commercial success depends, not so much on the completeness with which the two materials may be separated, as upon the handling of the material in such manner that all portions of the surface may make contact with the electrolyte, and so that the current may be utilized efficiently in removing the tin. Fig. 3 is from a photograph of a piece of sheet iron, from which the tin had been removed in about three minutes' time in a sodium nitrate solution, the iron having been so completely cleaned and protected from corrosion that the markings produced by the flow of metal during the process of rolling are clearly defined.

There is a considerable demand for a method of stripping nickel from iron-plated surfaces to succeed the expensive grinding operation, now necessary when an imperfect or worn-out nickel surface is to be replaced, and also for removal of nickel from the suspension rods and baskets. The nitrate solution cannot, however, be used for this purpose as the nickel and cobalt resist the action of the solution in about the same degree as does iron. Yet experiments have shown that while the nickel is not corroded, a thin layer of it may be removed from an iron surface by its long-continued use as the anode through a mechanical separation of the layer of nickel from the underlying iron. This seems to be due to the liberation of the gas within the pores of the metal which forces its way beneath the layer of nickel, thereby effecting the separation.

The chemical reactions which take place in the operation of the process for the removal of brass from iron are as follows: The electrolytic cell consists of a composite anode of copper, iron and zinc; a cathode of iron, copper, or other suitable metal; and an electrolyte of sodium nitrate dissolved in water. The passage of current causes a decomposition of the sodium nitrate into Na, which appears at the cathode, and $NO_3$, which is attracted to the anode, and at that point unites with the copper and the zinc to form soluble copper nitrate, $Cu(NO_3)_2$, and zinc nitrate, $Zn(NO_3)_2$. The sodium liberated at the cathode unites with the water to form NaOH and H, in accordance with the equation,

$$Na + H_2O = NaOH + H \qquad (1)$$

The hydrogen, instead of being liberated as a gas, acts as a reducing agent on the sodium nitrate, reducing it first to sodium nitrite

$$2H + NaNO_3 = NaNO_2 + H_2O \qquad (2)$$

and then reducing further in accordance with the equation

$$4H + NaNO_3 = NaNO + 2H_2O \qquad (3)$$

and the final reduction may be represented by,

$$NaNO_3 + 8H = NaOH + 2H_2O + NH_3 \quad (4).$$

If the hydrogen were liberated, as it would be in the case of a sulphate, not reducing the sodium nitrate, the action of the cell would be of the utmost simplicity. The soluble copper and zinc nitrates formed at the anode would diffuse and react with the cathode, NaOH precipitating the metals as hydroxides, and re-forming the original sodium nitrate.

By the reactions represented by equations (2), (3) and (4) free alkali and ammonia are liberated and the neutralization requires a certain amount of nitric acid as represented by equation

$$NaOH + NH_3 + 2HNO_3 = NaNO_3 + NH_4NO_3 + H_2O \quad (5).$$

The ammonium nitrate thus produced acts in a manner similar to the sodium nitrate in its dissolving action at the anode, and the process is therefore continuous, provided a suitable amount of nitric acid be added from time to time.

It has been found experimentally that the current when caused to flow at a density not exceeding ten to fifteen amperes per square foot of brass surface, will expend itself almost entirely in removing the brass, and little of the current will be wasted by flowing from the iron. The theoretical rate at which copper will be dissolved is 1.18 grams per ampere-hour, and the rate for zinc is 1.21. The brass, therefore, should be dissolved at a rate of about 1.2 grams per ampere hour, and under practical conditions of working this rate has been realized closely, the efficiency usually being between 75 per cent and 100 per cent. Each ampere hour will, according to the equation (1), liberate .037 grams of hydrogen. From equations (4) and (5) may be determined the amount of nitric acid necessary to neutralize the reducing action of this hydrogen, giving .59 grams of acid per ampere hour. Inasmuch as commercial nitric acid has a content of about 60 per cent $HNO_3$, the amount of commercial nitric acid required for each ampere hour will be in the neighborhood of one gram.

An interesting experiment illustrating the effect of the passive condition of iron is the following. If a clean iron sheet be dipped in a copper nitrate solution the iron becomes coated with a thin layer of copper by the so-called process of simple immersion. If, however, the iron be connected to a source of pressure, so that it immediately becomes the anode when dipping it into the copper nitrate solution, the deposition of copper upon it is prevented even after the current has been subsequently interrupted. Another method for illustrating the non-activity of the passive state consists in rendering the iron passive by use as the anode in a sodium nitrate solution, and then immersing it for a moment in a copper nitrate solution. If the surface thus wetted be scratched by a knife point, or by contact with a copper wire, the precipitation of copper commences, and spreads almost instantly over the entire surface of the iron plate.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

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## THE RARE ELEMENTS.

BY VICTOR LENHER, PH. D.

The term "Rare Element" in these days is applied, as a rule, rather loosely, and indeed it is a hard matter to draw a line which will be even approximately logical.

The quantitative distribution of the elements in the crust of the earth from our best and most recent calculations leads us to believe that the element titanium is more plentiful than our common carbon or sulphur, yet to the most of us familiarity with the knowledge of titanium is not to be classed with that of these other two elements, which are not so abundant in nature.

On the other hand, from the view point of the commercial value of the elements, or their compounds, the question of an economical method of extraction or demand and use largely enters as a factor. Not many years ago tellurium was quoted at several hundred dollars a pound, while to-day it can be bought for five dollars or less a pound.

Again, some of the more familiar elements are extremely difficult to obtain in elementary condition, such as, for example, fluorine, and our knowledge of this element has quite recently been much enriched through the work of Moissan.

From what sources the elements which as yet are unknown to us will appear, is largely a matter of conjecture. Whether some of the rare elements of the present day will break down into simpler forms, as has didymium, or whether they will come to us like helium, the atmospheric gas whose spectrum was known in the solar chromosphere before it was discovered on our own planet, can be only speculation. We indeed have to-day the spectrum of elements in the sun of which we have no terrestrial knowledge, and if they ever appear on our own earth it is not likely that they will be plentiful.

When a new element appears its properties and relations are eagerly investigated, usually by a large number of scientists, and its chemistry is subjected to the keenest of criticism. More than the usual amount of interest has centered around the new radioactive elements, one at least of which has had its elementary character fairly well established, and this interest has been brought about not only from the interesting new physical and chemical phenomena they present, but from the observations of experimenters like Ramsay, Soddy, Giesel and Bodlaender that the radiations of radium give off gases whose spectra show the lines of hydrogen and helium, and from the observation by Curie of the elevation of temperature which

radium develops. Of the radioactive elements, radium is the only one which thus far has yielded compounds of a sufficient degree of purity to warrant it being classed as an element. From the chemical side it much resembles barium. It, like polonium and actinium, occurs in pitchblende. Polonium is analogous to bismuth and from the bismuth products with which it appears, it may be obtained by fractionation. Actinium is closely allied to thorium, from which so far it has been impossible to separate it.

Other new radioactive bodies have considerable claims to recognition, and among these mention should be made of the radioactive lead of Giesel, Hoffman and Strauss, and the radiotellurium of Marckwald.

While pitchblende or uraninite has been more largely used as a source of radium, a number of other uranium and thorium minerals also contain these radiferous bodies.

The pitchblende from which most of the radium preparations have been obtained is worked up at the Joachimsthal mine in Bohemia. Many thousand tons of uranium residues are necessary to produce a pound of radium, and thus far only a very small quantity of pure material has been obtained.

In order to extract the radium from pitchblende, the residue from the sulphuric extraction of the ore for uranium is worked up by eliminating the other metals which are present by treatment with a boiling concentrated solution of soda, then with hydrochloric acid. From the hydrochloric acid solution the polonium and actinium are obtained, while the insoluble residue contains the barium and radium as sulphates. The radium is usually separated from the barium by means of the difference in solubility of the chlorides, radium chloride being less soluble than barium chloride.

The Curies use both fractional crystallization from water containing hydrochloric acid and fractional precipitation by alcohol. Giesel separates the radium from the barium by fractional crystallization of the bromides from water.

From the purest radium chloride obtained, radium shows the atomic weight of 225.

The salts of radium, such as the chloride, nitrate, carbonate and sulphate, when freshly prepared resemble the corresponding barium compounds, but they generally become colored. They are all luminous in the dark.

The radiations which emanate from radium are of three kinds. The "α" rays, which constitute the major proportion of the rays, produce the greatest portion of the ionization of gases, and they are by far the most energetic of the rays. They are, however, readily absorbed, and a thin sheet of metal will cut off the most of them. The "B" rays are likely longer waves; at all events, they are much more penetrative. They are readily deflected by the magnet. The "X" rays possess the greatest penetrative effect of any, and will excite or produce radioactivity through the air several feet away. They are unaffected by the magnetic field.

The characteristic actions of these various rays can only be touched on here. They cause fluorescent and luminous effects in many instances, such as barium platinocyanide and zinc sulphide. The diamond under the action of radium becomes phosphorescent, and may be readily distinguished from imitations.

The physiological action of the rays are such as to cause blisters similar to a scald. W. J. Hammer states that in a conversation with Professor Curie, the latter said he would not care to trust himself in a room with a kilo of pure radium, as it would doubtless destroy his eyesight and burn all of the skin off his body, and probably kill him.

The new atmospheric gases, *helium, neon, argon, krypton* and *xenon*, are characterized by their great chemical inactivity. No definite compound has been prepared with any of them. Their atomic weights, which are given as He, 4; Ne, 20; A, 40; Kr, 82, and X, 128, have been determined from their densities, the gases being assumed as monatomic. These gases are all present in our atmosphere; neon, krypton and xenon are best obtained by the fractionation of liquid air. Argon is obtained from atmospheric nitrogen by absorbing the nitrogen by means of hot metallic magnesium, or by passing induction sparks through a mixture of air and oxygen over caustic potash when the oxygen and nitrogen unite and combine with the potash, leaving the argon.

Helium, whose presence in the sun was detected by Lockyer in 1868, is found in small quantities in the atmosphere. Its principal sources are certain rare minerals, such as pitchblende, monazite, samarskite and columbite, from which it may be obtained by heating or by treatment with dilute sulphuric acid.

It is interesting to note that a number of mineral springs give off gases which contain more or less of these gases. Recently the gases from certain springs in France and Spain have been carefully examined, and have been found to contain mainly nitrogen along with from 0.9 to 1.8 per cent of argon.

In the alkali group of metals we have *lithium, rubidium* and *caesium*. Lithium is perhaps the most important on account of the use of its salts in medicine. Its most important natural sources are the minerals triphyllite, a triple phosphate of iron, manganese and lithium, zinnwaldite and lepidolite, which are lithia micas, spodumene and other silicates and phosphates. These minerals carry from one to ten per cent of lithia. Nearly 2000 tons of lithium minerals are annually produced in the United States, the New England States, North Carolina, South Dakota and California, producing practically all of the lithia minerals. Over a third of the lithia salts used in the United States are imported.

The crude minerals are valued at about $20 per ton, the valuation being according to the lithia content. The refined salts average a little over $1 per pound. The principle made use of in the extraction of lithia from its minerals is the formation of an insoluble carbonate in strong solution. After fusion and sudden cooling by water, the silicates are pulverized and attacked by hydrochloric acid. The silica is removed by evaporation to dryness, the iron, aluminium, calcium, magnesium, etc., are removed by precipitation with sodium carbonate, after which the clear liquid is evaporated to a strong solution from which more sodium carbonate precipitates lithium carbonate. Inasmuch as lithium forms a very soluble urate, the salts are used extensively in medicine for the removal of uric acid from the system, the carbonate and citrate being used more extensively than the other salts. While lithium imparts a crimson color to the flame, thus far the salts have been little used in the manufacture of firewroks, due largely to the fact that strontium compounds, which also color the flame red, are much cheaper.

Rubidium and caesium in their chemical characteristics much resemble the more common alkali metals, but are much more active. They frequently occur in very small quantities in the minerals which carry the alkalis. While many mineral waters contain these elements in small quantities, the lithium minerals, as a rule, are more important sources. The rare mineral pollux is a hydrous silicate of aluminium and caesium which contains from 13 to 37 per cent of caesium oxide. From pollux, Chabrie extracts caesium by decomposing with hydrofluoric acid, freeing the solution from the heavy metals, treating with ammonium carbonate and evaporating to dryness. The residue, when extracted with boiling alcohol, yields caesium carbonate which is soluble.

Caesium and rubidium are best separated by treating a chloride solution with $SnCl_4$ or $SbCl_5$ when the insoluble caesium double salt is found.

The metals are obtained by heating the hydrates with aluminium, or the carbonates with magnesium. No practical use has thus far been made of these metals or of their compounds.

In the alkaline earths group of metals, *beryllium*, whose chief sources in nature are beryl, chrysoberyl, phenacite, euclase and some more rare silicates, stands between calcium and aluminium, in its general properties very much resembling

both in certain ways. Thus far, neither metallic beryllium or its compounds have had any practical uses; in fact, the methods for the preparation of the metal have hardly received the attention which are warranted by an element which is so like aluminium. The metal can be obtained by reduction of the chloride with sodium at a red heat, or by heating the oxide with magnesium. The specific gravity of the metal is about 2 (its specific gravity varies from 1.64 to 2.1, according to the observer). It does not decompose water, and remains unchanged in the air. It is white and ductile, and can be rolled into sheets. These properties, as given to us, would lead us to believe that its commercial side certainly needs closer investigation. Many of the natural beryllium compounds, as chrysoberyl and the emerald, are valuable as gems, but outside of the uses in scientific investigations beryllium compounds are not in demand. In order to extract beryllium, the minerals are either fused with the alkaline carbonates or with potassium fluoride. In either case the fusion is treated with sulphuric acid. In the alkaline carbonate fusion the silica is volatilized as gaseous silicon fluoride. The aluminium, which is usually present in large amount, is then crystallized out as the potassium alum, after which the beryllium is separated by the addition of the solution to a saturated solution of ammonium carbonate. Beryllium forms a soluble double carbonate with ammonium carbonate, which is decomposed by the addition of hydrochloric acid, after which the hydrate can be precipitated by ammonia and the oxide obtained.

*Gallium*, *indium* and *thallium* are of a pronounced metallic character, the first two are very rare, and both occur not infrequently in certain zinc blendes.

The Bensberg zinc blende is the richest source of gallium, and it contains only 16 milligrams of gallium per kilo. The Freiberg blende carries small amounts of indium, from 250 to 1000 milligrams per kilo. A large number of iron ores have been found by Hartley and Rammage to contain gallium and indium. The principle involved in the extraction of gallium is the precipitation of the metal from a neutral solution by means of metallic zinc. Metallic gallium has the very low melting point of 30° C, consequently can be melted in the hand. The characteristic reactions used in the extraction of indium are the precipitation of the metal by means of zinc from a neutral solution and the formation of an insoluble basic sulphite. Neither gallium or indium, or their derivatives, have any commercial use, and thus far have only been of importance scientifically.

Thallium is considerably more plentiful than gallium or indium; it occurs not only in the zinc blendes, but also in iron pyrites, in natural waters, in several of the micas, and in a few very rare minerals which are essentially thallium compounds. One of the principal sources of thallium is flue dust from the manufacture of sulphuric acid. This flue dust is, according to Crookes, leached with boiling water, the chloride precipitated by hydrochloric acid; this chloride is transformed into sulphate by means of concentrated sulphuric acid; the sulphate is purified from other metals by first treating with hydrogen sulphide, then with ammonia. The metal is obtained from the solution either by the electrolysis of the sulphate or by means of metallic zinc. From three tons of flue dust Crookes obtained 68 pounds of impure thallous chloride.

Metallic thallium is very heavy, has a specific gravity of 11.9, oxidizes readily in moist air, forming thallous hydroxide, which is soluble in water, consequently if thallium is partially immersed in water, is allowed to stand exposed to the air, it will slowly dissolve. Two states of oxidation are known with the element, the thallous ($Tl_2O$) being the most stable. The thallic salts ($Tl_2O_3$) are quite readily reduced to the thallous. The best method for the precipitation of thallium for analysis is as the yellow insoluble thallous iodide.

Thallium finds considerable use in the manufacture of optical glass. Thallium glass possesses a very high refracting power, more so than lead glass. In addition to the use of the thallium glass for optical purposes, it is also used for the manufacture of artificial gems. Ordinarily thallium can be bought for $10 to $12 per pound.

*Germanium*, in its chemical characteristics, stands between silicon and the stannic compounds. It is found in a few rare minerals in certain silver ores. The element is quoted by chemical dealers at a very high price per gram, about $70. It has no practical uses at present, but has been of great scientific interest as the element, and the properties of a number of its compounds were prophesied by Mendeleef before its discovery, and the predictions were later fulfilled in a remarkable manner.

*Titanium* is nowadays considered as one of the common of the elements. Its applications in electrometallurgy by Rossi have attracted wide attention. A recent description of the manufacture of ferro-titanium will be found in this Journal in Nov., 1903. The occurrence of titanium in iron ores and of the oxide in native condition need only be mentioned as abundant sources of this element at this time. The production of the metal by the electric furnace method in a fairly pure condition has been ably demonstrated by Moissan.

The chemical compounds have not yet received the attention that they deserve. We have, however, a few uses developed recently for titanium salts which bid fair to give promising results. Dreher has recommended the dyeing of all kinds of fibre, as well as leather, to deep shades by the uses of titanium salts along with metallic tannates. Titanium potassium oxalate is used along with aluminum acetate, the oxide of titanium being precipitated on the fibre with the dyestuff as a lake.

The trichloride of titanium is a powerful reducing agent: it reduces sulphur dioxide to sulphur, copper sulphate to metal, nitrogroups to amines, etc. The sesquisulphate is also a strong reducing agent; it is obtained electrolytically as a commercial article and comes in the market as a sodium sulphate double salt. It is very likely that the chemical and metallurgical side of titanium will receive far more attention in the next few years than it has in the past, particularly in view of the many promising results which have thus far been obtained.

Department of Chemistry, University of Wisconsin, Madison, Wis.

(*To be concluded.*)

## ELECTRICAL LOSSES IN AN ELECTROLYTIC COPPER REFINERY.

BY CARY T. HUTCHINSON, PH. D.

The article in the December number of ELECTROCHEMICAL INDUSTRY, by Mr. Benjamin Magnus, recalls to the writer a series of investigations made in the winter of 1897 at the same refinery, for it is easily identified as that at Anaconda. A comparison of the results obtained by Mr. Magnus, presumably showing present conditions, and those obtained five years ago, illustrates forcibly how slowly improvements come about in electrolytic copper work. This seems to be due chiefly to what is politely styled "conservatism" on the part of those in charge and to their abnormal foundness for secrecy, in a matter where secrecy is utterly absurd, since there is nothing to conceal.

The following figures were obtained in the course of an investigation covering the cost of producing and using steam power throughout the Anaconda works, and also of determining the cost of electrolytic refining at these works. The energy loss in contacts in the tanks, obviously great, was considered in detail. More than a thousand separate measurements were made with milli-voltmeters, and the results given below are the average of these measurements.

Beginning at the generator terminals, the losses may be divided into, (1) switchboard loss, including all losses from generator terminals to the beginning of the feeders to the tanks; (2) loss in the feeders, including only the loss to the tank mains; (3) loss in the mains on the tanks; each tank, as described by Mr. Magnus, has heavy copper mains, upon which

the anode and cathode bars rest; (4) loss in the various contacts from the end of the feeder to the solution; these losses in contacts include, (a) joint between feeder and tank main; (b) contact between anode bar and main; (c) contact between anode hook and anode bar; (d) contact between anode hook and anode plate; (e) contact between cathode plate and cathode bar; (f) contact between cathode bar and negative main.

Without going into the details of these measurements, the results for one "system," comprising two hundred tanks in series, were as follows:

| | | | |
|---|---|---|---|
| Currrent | | | 3800 amperes |
| Pressure at generator | | | 67 volts |
| Losses: | | | |
| (1) In switchboard | 0.31 volts | = 0.46 | per cent |
| (2) In feeders | 2.00 " | = 3.0 | " |
| (3) In mains | 6.00 " | = 9.0 | " |
| (4) In all contacts | 7.36 " | = 11.0 | " |
| | 15.67 " | = 23.5 | " |

From these figures, the electrical efficiency from generator terminals to the solution becomes 76.5 per cent, and the total loss from generator to the solution is divided as follows:

| | | |
|---|---|---|
| (1) In switchboard | 2.0 | per cent |
| (2) In feeders | 12.8 | " |
| (3) In mains | 38.4 | " |
| (4) In contacts | 46.8 | " |
| | 100.0 | " |

The loss in tank contacts at 3800 amperes was 7.36 volts, and, therefore, at 4000 amperes, the loss would have been 7.7 volts = 0.0385 volts per tank. The corresponding figures given by Mr. Magnus is 0.0510 volts per tank. Hence, in the last five years there has apparently been an increase of some 35 per cent in the contact resistances, which were, even at that time, excesssive. This drop is unaffected by the number of plates in the tank, as long as the current density is unchanged, which is practically the case.

Deducting the loss in switchboard, feeders and mains, the voltage at the tanks was then 58.7 for 200 tanks = 0.293 volts per tank. It is now given as 0.23 volts per tank. This, of course, is a much needed improvement, and brings this refinery in line with other refineries operating in multiple. It has probably been effected by putting the plates closer together, and, possibly, by some much needed changes in the solution then used.

It is interesting to compute the cost of this loss, and to show the magnitude of the possible economies. For one tank system of 200 tanks, the loss amounts to 60 kilowatts; the cost of the power at that time, not including any charges for depreciation or interest, was $157 per kilowatt, per year of 8,760 hours. This makes the total annual cost of the wasted energy for one tank system $9400, and for the six, $56,400. As the capacity of the refinery was approximately 30,000 tons per annum, this gives a cost of $1.88 per ton for lost energy. While this amount seems small, it is very approximately equal to the interest on the total investment in the refinery plant; hence, a saving of one-half of this loss would justify an increase of 50 per cent in the total investment. As a matter of fact, one-half of this loss can be saved for a very much smaller sum. The increase of 35 per cent, shown by Mr. Magnus' figures, means an added cost of about $10,000 per annum, if the cost of energy is the same as it then was.

A comparison was made at the same time between the operation of this plant and a plant using a series system. The table below gives certain figures of interest, showing the relative cost:

| | System. Multiple. | Series. |
|---|---|---|
| 1. Generator capacity per ton output per day | 15.8 kw. | 9.0 kw. |
| 2. Floor space required per ton output per day | 830 sq. ft. | 375 sq. ft. |
| 3. Copper produced per kw.-hour | 7.25 lb. | 9.6 lb. |
| 4. Time copper is held in tanks | 30 days | 15 days |

It would be a natural supposition that the conditions of operation in an electrolytic refinery are practically uniform; yet one of the most conspicuous facts in the operation of this refinery was the great irregularity in the results. Taking, for instance, as a criterion, the ratio of coal burned to copper produced, the figures for ten successive months were as follows:

| | Ratio of Coal Used to Copper Produced. |
|---|---|
| January | 2.09 |
| February | 2.17 |
| March | 1.82 |
| April | 1.61 |
| May | 1.46 |
| June | 1.98 |
| July | 1.01 |
| August | 1.22 |
| September | 1.04 |
| October | 1.25 |
| Average | 1.60 |

Here was shown a variation of more than two to one betweenthe best and poorest performance, with no means of accounting for the difference. This is only a sample of the conditions then existing in the largest copper refinery in the world. It shows what undue secrecy and refusal to compare results with others leads to.

## APPARATUS FOR NICKEL AND COPPER ANALYSIS

By David H. Browne.

A convenient device for the use of storage battery and intween the best and poorest performance, with no means of and nickel, is that devised by the Northern Engineering Company of New York. It was desired to use the electric light circuit of 110 volts at night, in connection with a storage battery; with an automatic switch so arranged as to furnish an uninterrupted current. Further, the current was to be so divided as to furnish a steady flow of 0.4 amp. to the nickel plating, and 0.2 amp. to the copper plating frames; together with an independent circuit to an experimental frame, which was to have as strong a current as might be desired.

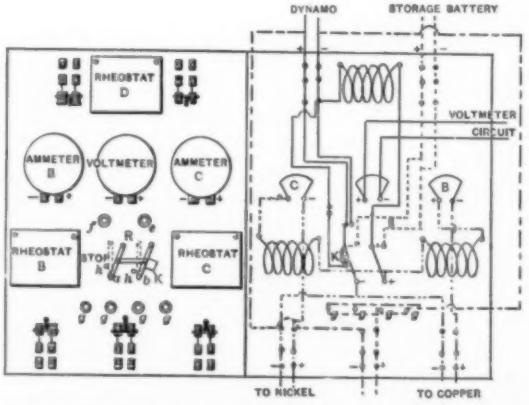


FIG. 1.—SWITCHBOARD, THE LEFT SIDE OF THE DIAGRAM SHOWING THE FRONT, THE RIGHT SIDE THE BACK.

The panel is 36 in. wide and 46 in. high. The electric lighting circuit enters at the back and passes through the rheostat *D* to the double pole switch *R*, at which point the current

divides. One part passes to the right, enters the rheostat *C*, and flows through the ammeter *C* directly to the nickel plating frames. The current is cut by this rheostat to 0.4 amp., and passes in series through the individual anodes and cathodes on the plating frames and returns on the negative side at the base of the switchboard, through the two-pole switch *R*, and so back to the lighting circuit.

Following the other branch of the positive lead the current passes through the rheostat *B*, where it is cut to 0.2 amp., and passes through the ammeter *B* to the copper plating frames from which it returns on the negative side at the base of the switchboard to the two-pole switch and back to the dynamo.

A branch from the negative side of the lighting circuit

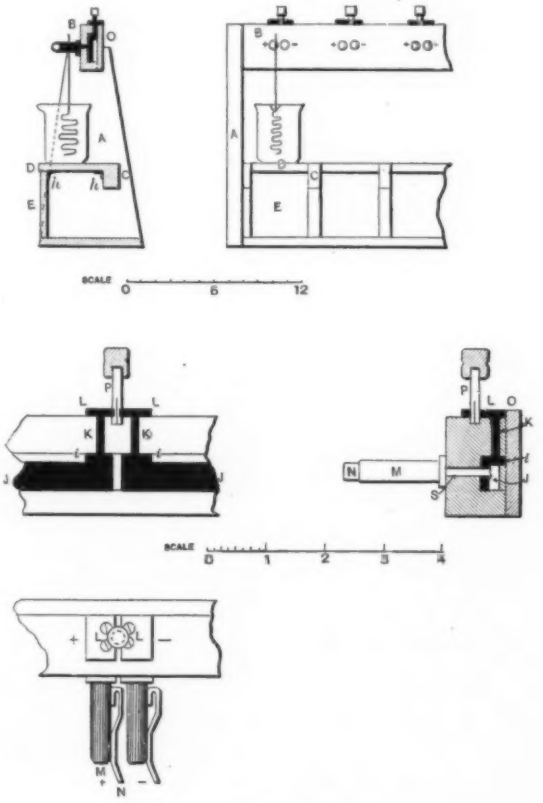


FIG. 2.—PLATING FRAME.

passes around the iron block *K*, forming an electro-magnet which attracts a pole piece secured to the arm *b* of the switch *R*. As long as the electric current passes this magnet holds the arms *a* and *b* in the position shown, and makes all the electrical connections as described.

If the dynamo is shut down the magnet *K* loses its strength, and a spring at the base of the switch *R* comes into play, throwing the switch to the left, as shown by the dotted lines. This cuts out the lighting circuit and throws in a storage battery circuit shown by the dotted wires at the back of the panel. When the dynamo starts again, the magnet overpowers the spring and automatically draws the switch into its original position.

In case any of these instruments should get out of order, an entirely independent lighting circuit is carried to the four lamps, *G, G, G, G*, at the base of the panel, from which a current regulated by the number and size of the lamps can be temporarily connected to either circuit. This can also be used on a separate frame for experimental purposes.

The plating frame consists of a hardwood horizontal piece, *B*, hollowed out at the back to receive the copper conductors *J*. which are covered in by the back piece *O*.

Below and at the back of the frame is a second horizontal strip, *C*, to which are hinged the tables *D*, which are supported by the foot *E*, which is hinged to the table. When a beaker is to be removed from the frame, the foot is pushed back, which allows the table to fall.

The electrical connections consist of a series of short copper bars, to each end of which is soldered an L shaped lug, *i*. Through this lug passes a bolt, *K*, which connects the ends of the copper bars with the cut-out switch *L*. The pin *P*, when placed between the terminals of the switch, cuts out the cathode and anode clamps *M*.

These clamps are of aluminium, and are connected to the copper bars *J* by a screw, *S*. When the pin *P* is taken out, these clamps receive the current which thus passes in series from one plating beaker to the next.

The platinum anodes and cathodes are slipped from the front between the aluminium bar *M* and the brass spring *N*. This holds the electrodes firmly in a notch and avoids cutting the wires by screws, as is the case with the ordinary plating frame.

This apparatus has been in use at the Orford works for nearly two years and has given entire satisfaction.

## ELECTRICITY DIRECT FROM CARBON.*

By Prof. Richard Lorenz, Ph. D.

By far the greatest part of the energy which is changed into useful work for the various purposes of engineering and human life, comes from the chemical energy of burning carbon. The energy reservoir, given us by nature in the form of carbon deposits, is not inexhaustible. We should, therefore, endeavor to utilize the coal we have to the best advantage. The efficiency of steam engines and gas engines is necessarily small. We now have, no doubt, a number of possible methods for improving the efficiency of the machines; we may refer, in this connection, to the construction of the steam turbine. On the other hand electrochemistry gives us points of view from which a still more perfect utilization of the energy of carbon appears possible. These new points of view are contained in the theory of galvanic cells, and our problem is to design what is commonly called a carbon cell.

We may start with some introductory remarks on the thermodynamics of the subject. From any process which goes on voluntarily in nature, mechanical work may be derived, if we let this process take place in a suitable device ("machine"). The external work becomes a maximum if we succeed in making the process isothermic and reversible at any moment. Under these conditions the process gives the maximum of external work which it is possible to give under any circumstances.

Helmholtz calls that part of the change of the total energy of an isothermic process which can be changed into external work, vis viva, etc., the change of the "free energy" of the system. The difference of the change of total energy, and of the change of free energy is called by him the change of the "bound energy" of the system.

The view of Thomson that the heat of reaction, corresponding to a chemical process, can be changed completely into electrical energy (Thomson's rule), has been found to be not correct since an electrochemical system tends to become warmer or cooler, while its chemical energy is changed into electrical energy, so that if the process is to be isothermic, heat is either to be given off to the surroundings from the cell or to be supplied from the surroundings to the cell.

From the first principle of thermodynamics we get the relation $U = A - Q$, in which U represents the decrease of total energy, A the work done by the system, and Q the heat supplied from the outside to the system. Each of these quantities may be positive or negative.

*A paper read before the Physical Society of Zuerich. Translated and slightly abstracted from the Mitteilungen of the Society.

From the second principle of thermodynamics we get the relation

$$dA = Q\frac{dT}{T}$$

and by combining these two relations we get the "Gibbs-Helmholtz equation"

$$A = U + T\frac{dA}{dT}$$

The maximum work (A) which an isothermic process can accomplish, equals the decrease of total energy (U) plus the product of the absolute temperature (T) and the temperature coefficient $\left(\frac{dA}{dT}\right)$ of the capacity of the system to do external work.

The great importance of this equation is shown in its application to chemical and electrochemical reactions. The question is whether we can design systems in which the maximum of external work can be obtained. This is really possible if the chemical reactions are used in galvanic cells to generate electrical energy. In this case the external work which appears in form of electrical energy is $e\ n\ F$, where $e$ is the e. m. f., $n$ the chemical valence and F the constant in Faraday's law. $e\ n\ F$ is the free molecular energy of the system. The Gibbs-Helmholtz equation thus assumes the following form[1]:

$$enF = U + \frac{Td(enF)}{dT} \text{ or } e = \frac{U}{nF} + T\frac{de}{dT}$$

To show the application of this formula we give the following examples which prove that Thomson's rule in its original conception is not correct, and which also show that galvanic cells represent systems which, according to their constitution, can transform the chemical energy of exothermic or endothermic reactions, with greater or smaller efficiency, into electrical energy.

As first example, we take the reaction,

$$CuSO_4aq + Zn = ZnSO_4aq + Cu + 25{,}055 \text{ calories.}$$

This[2] is a reaction in the Daniell cell Zn, $ZnSO_4$, $CuSO_4$, Cu. According to Thomson's rule we expect electrical energy corresponding to 25,055 calories. In fact, this is in this case nearly correct. We get the e. m. f., corresponding to 25,055 calories, = 1.08 volts, while the real e. m. f. is 1.093 volts, corresponding to 25,263 calories, so that the difference of the two quantities of heat is 207 calories.

The cell has therefore a very small temperature coefficient of e. m. f., and we may consider it to be practically zero, so that in this case Thomson's rule is practically correct.

A second case is.

$$2AgCl + Zn + aq = ZnCl_2aq + 2Ag + 26{,}023 \text{ calories.}$$

This is the reaction of the cell Zn, $ZnCl_2aq$, AgCl, Ag.

In this case we get the e. m. f. which would correspond to the heat of reaction ($U/_2 = 26{,}023$ calories) = 1.12 volts. The e. m. f. which the cell really has is e = 1.01 volts, corresponding to 23,453 calories. We therefore get

ing to 23,453 calories. We therefore get $\frac{Tde}{dT} = -0.11$ volt,

which corresponds to Q = — 2,570 calories. Since Q means the heat supplied from the surroundings to the cell, we have, in this case, a loss of heat from the cell to the outside. The cell, while working, tends to heat up[3], and if the temperature is to be maintained constant heat is to be given off from the cell to the surroundings. This means that the chemical energy of the reaction is not completely changed into electrical energy, but partly (about 90 per cent) into electrical energy and partly into heat. The efficiency (giving the electrical energy produced in per cents of the chemical energy lost) is therefore 90 per cent. This represents the maximum limit of the efficiency which a cell of this type can have.

A third case is the reaction

$$Pb + Cu(CH_3COO)_2 = Pb(CH_3COO)_2 + Cu + 8{,}766 \text{ cal.,}$$

which is the reaction of the cell Cu, $Cu(CH_3COO)_2$, $Pb(CH_3COO)_2$, Pb.

We have in this case $\frac{1}{2}U = 8{,}766$ calories, corresponding to 0.37 volt, while the e. m. f. in reality is e = 0.47 volt, corresponding to A = 10,842 calories.

We therefore have for the difference Q = 2,076 calories and $\frac{Tde}{dT} = +0.10$ volt. In other words, instead of an e. m. f. of 0.37 volt, which we should expect from Thomson's rule, we get in this case an e. m. f. of 0.47 volt, which is more than corresponds to the heat of the chemical reaction. In this case, while the cell works it tends to cool, so that if its temperature is maintained constant, heat must be supplied from the surroundings to the cell. The chemical energy of the reaction in the cell, together with the heat supplied from the surroundings to the cell, are changed into electrical energy, so that we get in this case an efficiency beyond 100 per cent; namely, 123 per cent, if the efficiency is defined as the electrical energy produced in per cents of the chemical energy consumed.

The chemical reactions which we have so far discussed for changing chemical energy into electrical energy were so-called exothermic processes; that is, such chemical reactions which develop heat while they are going on. There are, however, numerous chemical reactions, in which heat is absorbed from the surroundings, and they are called endothermic processes. One of the most interesting results of experimental chemical thermodynamics is the successful proof that it is indeed possible to utilize endothermic chemical processes for performing external work, while, according to Thomson's rule, it should be impossible to obtain any work if the heat of reaction is negative. Nernst and Bugarsky have found, for the first time, such an example, the chemical reaction being

$$HgCl + KOH = \tfrac{1}{2}Hg_2O + \tfrac{1}{2}H_2O + KCl - 3{,}710 \text{ calories.}$$

This is the reaction of the cell Hg, HgCl, KCl, KOH, $Hg_2O$, Hg.

In this case we have

$U/_2 = -3{,}710$ calories, corresponding to — 0.14 volt, while the e. m. f. is in reality e = + 0.32 volt, corresponding to A = 7,566 calories. Hence, for the difference we get Q = 11,276 calories. In this case, while the reaction goes on at constant temperature, heat is supplied from the surroundings to the system, and this heat is partly used up in supplying the heat of chemical reaction and partly changed into electrical energy[4].

After having thus discussed the thermodynamical foundations of the theory of galvanic cells, we will now take up the problem of getting electricity direct from carbon.

It would be possible to obtain the maximum external work corresponding to the reaction

$$C + O_2 = CO_2 + 97{,}650 \text{ calories}$$

[1] In this equation $e$ is measured in volts, $n$ is the change of chemical valence (a pure number), F is the electric charge of a univalent gramion (96,540 coulombs). U is the change of chemical energy, if the chemical symbols in the equation representing the process mean gram-molecules or gramatoms,and is assumed to be measured in joules. If U is given in gramcalories (as is usually the case), its value is to be divided by 0.24, and the above equation assumes the form $e = 0.000\,043\ U/n + T\frac{de}{dT}$. Of course, T is the absolute temperature (or degrees centigrade + 273), for which the cell has the e. m. f. $e$, while $\frac{de}{dT}$ is the temperature coefficient of the e. m. f.—*Translator.*

[2] 25,055 calories is the heat corresponding to the reaction, if in the above equation each chemical symbol represents one-half grammolecule. Since the change of valence is here two, 25,055 valories represents the quantity U/n in the last equation of footnote 1.—*Translator.*

[3] This is, of course, not Joulean heat, but heat which would appear even if we could design the cell so that the Joulean heat becomes negligible.—*Translator.*

[4] While, from Thomson's rule, one would expect that the above reaction would require the expenditure of 0.14 volt, to be impressed from an external source to the terminals of the cell, in reality the cell acts as battery, and has an e. m. f. of 0.32 volt.—*Translator.*

in form of electrical energy if we could render the burning of carbon in a galvanic cell an isothermic and reversible process. According to Nernst (*Theoretische Chemie*, page 639) we can make calculations which show that the oxidation heat of carbon at ordinary temperature (U = 97,650 calories), may be changed nearly completely into external work. Theoretically we find the maximum amount of external work which we can derive from the reaction as A = 91,470 calories. It also follows that the efficiency of the carbon cell must be the smaller the higher the constant temperature at which it operates. For the e. m. f. at ordinary temperature we get 0.99 volt for the oxidation of C to $CO_2$, while we have the e. m. f. 1.41 volts at 18° C. for the oxidation of CO to $CO_2$, and 0.57 volt for the oxidation of C to CO (Bucherer, *Elek. Zeit.*, 1895, pages 502 and 597; Luther, *Zeit. f. Phys. Chemie*, vol. 36, page 385).

These theoretical values appear quite favorable to a carbon monoxide cell, since it gives theoretically a considerable higher e. m. f. than the combination of carbon and oxygen with the formation of carbon dioxide. Of course the former cell, while giving a certain number of ampere hours, consumes twice the quantity of carbon consumed in the latter cell. The former cell would also have some technical advantages, for instance, the easier preparation of pure carbon monoxide gas, while the impurities in carbon or coke would be the cause of many technical difficulties. However, it must be emphasized that the question whether we have to attribute an electromotive force to carbon monoxide, has not yet been definitely settled, although it seems improbable if judged from preliminary experiments.

We may mention that up to the present we cannot say safely that there really exist carbon ions in sufficient concentration, that is, compounds of carbon with electrons. Any electrochemical processes depend on the formation, or the discharge of ions. Hence, the existence of such ions is the fundamental supposition for the validity of the above thermodynamical conclusions for the reason that the reversibility depends electrochemically upon the existence of ions.

It is true, experiments may be made in which carbon appears to show an electrolytic behavior similar to that of metals, for instance, zinc. Such experiments were made especially by A. Coehn. If a carbon anode is used in sulphuric acid of suitable concentration, the carbon goes into solution in form of a brown substance which appears to be similar to the anodic solution of a metal. The solution of carbon even takes place according to Faraday's law. Moreover, from such a solution a deep velvet-black carbon-like coating can be deposited on a platinum cathode, so that we seem to have a reversible process, similar to the case of metals.

These simple experiments, when published, appeared to justify at first sight the hope that it might be possible to dissolve carbon in a similar way as zinc, in a galvanic cell, so that the design of the required isothermic and reversible machine would have become possible. However, such expectations did not realize up to the present, for the following reasons.

First, in carbon electrodes we have never pure carbon, but they consist of hydro-carbons of high complexity. The products of anodic oxidation are mainly benzenehexacarboxylic acid, benzenetetracarboxylic acid, and hexahydrobenzenehexacarboxylic acid, which are substances found in brown coal deposits in combination with $Al_2O_3$. The first product is mellogen $C_{11}H_2O_4 + 1\frac{1}{2}H_2O$, which by further oxidation is changed into the above substances. (*Zeit. f. Elektrochemie*, vol. 4, page 63.) The black body which is deposited from the solution by electrolysis is not pure carbon, but a substance containing carbon, and also containing O and H. In this case we probably have in the electrolyte a migration of colloids and probably not of carbon ions. The analogy with the solution of metals is thus to be considered as quite limited (Haber, *Grundriss d. Technischen Elektrochemie*, page 182). On the other hand, recent calculations of Bodlaender concerning the solution of carbon have given a very remarkable and interesting result. When carbon is dissolved in aqueous solution we have the reaction

$$C + 2H_2O = CO_2 + 2H_2.$$

This is a process analogous to the solution of zinc with evolution of hydrogen. The calculation shows that the free energy A of this reaction in the case of carbon is negative and equal to 15,230 calories. If we want to dissolve carbon in dilute sulphuric acid, we must consume 0.16 volt. This agrees with the results of the experiments since Coehn found that the solution of carbon in dilute sulphuric acid takes place only under the application of an external e. m. f. The reason is that in this case we must develop hydrogen. If, by means of the solution of carbon we want to get electrical energy, we must use a depolarizer for hydrogen at the positive pole, in form of oxygen from the air, or in form of other oxidizing agents. By using lead peroxide, Coehn really got 1.03 volts with a current of 0.01 ampere. The application of air depolarizers involves various difficulties, which are increased in this case especially by the low speed of the solution of the carbon. If alkali would be used instead of sulphuric acid, the result would be somewhat more favorable.

Anyhow, from these considerations and investigations, it follows that the solution of the problem to get electricity direct from carbon is not theoretically impossible. The practical solution might be found by three different ways.

The first is to design a galvanic cell with carbon as dissolving electrode, hence, corresponding to the zinc in the Daniell cell. In the majority of suggestions of this kind it was proposed to use a carbon electrode in aqueous solution. But since the reaction velocity between carbon and oxygen at low temperature is very small, but somewhat higher at red heat, the use of a galvanic cell with a fused electrolyte seems more promising, although, as mentioned before, the efficiency will be the lower the higher the temperature. The first proposals were cells of the type

Fe, PbO, carbon; Fe, $KNO_3$, carbon;

but this type of cell is unsuitable, since the oxidizing agent is in direct contact with the anode, so that the carbon is consumed by local action, which does not represent the generation of electrical energy. Researches made in this direction have found a certain conclusion by the construction of the carbon cell of Jacques.

The Jacques cell consists of carbon, fused sodium hydroxide and iron. This proposal of Jacques was announced to the world with considerable advertising skill, yet the extended investigations of Reed, Liebenow and Strasser, Lorenz and Sacher have shown that the original opinion held by the inventor on the action of his cell, is wrong.

In order to demonstrate the Jacques cell, on a small scale, an iron crucible may be used in which sodium hydroxide is being fused. During this time the iron crucible becomes "passive," while at the same time the molten contents assume a brown color. If, now, a bright iron point is put into the fused mass and the iron point and crucible are connected together through a galvanometer, a current is observed which goes from the active iron point to the passive crucible. After a short time this current disappears, because the iron point also becomes passive. If a carbon electrode is suspended in the fused mass and connected with an active iron point through a galvanometer, a current is observed which originally goes from the iron point to the carbon (in the electrolyte). This cell therefore operates, then, at the expense of iron being dissolved. After a short time, however, this current decreases, the galvanometer needle passes through zero and a current of reverse direction is now observed, which, therefore, in the fused mass goes from the carbon to the iron. A current of this latter direction may be obtained from the start if the carbon electrode is connected with the passive crucible through the galvanometer. This current lasts and is produced by the solution of carbon. In this condition the system represents the Jacques carbon cell. (Lorenz, *Zeit. f. Electrochemie*, vol. 9, page 159.)

However, this cell is not a practical solution of the problem

of generating electricity direct from carbon, since the regeneration of the substances formed during discharge is expensive. Moreover, in all carbon cells which use carbon as dissolving electrode only the forms of carbon which are electric conductors, and which are expensive, can be used. Small amounts of impurities greatly influence the action of the cell. For this reason some inventors have used gases like carbon monoxide, illuminating gas, etc., for the design of carbon cells, since they can be obtained in a condition of greater purity. However, such gases contain no longer the whole caloric effect of the carbon.

In order to render such cells active, a gas battery must be constructed with an oxygen cathode and a carbon monoxide anode. Here the question arises whether the carbon monoxide can be electrochemically active since the existence of CO ions has not yet been proven. For the case of a carbonate as electrolyte a depolarizing action of carbon monoxide can be assumed, since it may combine with the $CO_3$ ions to form $CO_2$. The suggestion of Bucherer (German patent 88,327) uses this scheme, his cell containing a platinum tube as cathode, through which oxygen is conducted, and a cast iron and nickel tube as anode through which CO is conducted. It seems, however that the action in this cell is different from what the inventor assumes it to be. Borchers (U. S. patent 567,705) has devised a similar cell.

A second method of generating electricity from carbon by an electrochemical device does not intend to produce the maximum work which corresponds to the oxidation of carbon. In this case the energy of the carbon is utilized outside of the cell for regenerating the substances which have undergone a change during the discharge of the cell. Nernst (Bericht über die erste Hauptversammlung der *Deutschen Elektrochemischen Gesellschaft*, page 29) has expressed the opinion that since it is very difficult to transform the chemical energy of carbon directly into electrical energy, it might be possible to arrive at the same result by a roundabout way. For this purpose the energy of carbon is to be transformed into another chemical energy of such a form that it may be immediately utilized in a galvanic cell. To sketch the idea, one might use cells with a zinc anode, and might devise a reversible reaction by which the zinc salt, formed during discharge, is reduced by carbon. Such a cyclic process would also have a maximum efficiency, since all processes which go on would be reversible.

In such a method, however, a loss of free energy is necessarily involved, since the regeneration cannot be rendered absolutely reversible, especially as the salts which have been formed, very often cannot be reduced, or only with great losses.

The Daniell cell might be used in such a method and the zinc sulphate which is formed during discharge might be regenerated by means of carbon to zinc and sulphuric acid, while the deposited copper is rechanged into copper sulphate by means of the sulphuric acid and air. However, the economy of such regenerating processes is so low that it seems not feasible to utilize the energy of the carbon in this way. It might, perhaps, be easier to use for such a purpose the type of cells devised by Lorenz, in which the electrode metals are obtained in form of their hydroxides or oxides; this might seem more promising, because substances are here formed in the cell which are more easily reduced, although it cannot be denied that difficulties of various kind are here present, since irreversible processes probably go on while the cell gives current. Besides, it is questionable whether the practical application of this method would be easy and simple.

A third method of utilizing the energy of carbon is not to try at all to use it electrochemically, but to use it for producing purely caloric effects in combination with galvanic cells. If carbon is used for the simple regeneration of heat, the part of the heat which can be changed into work is limited by the second principle of thermodynamics, so that by this method we cannot transform the total free energy into useful work. Nernst has made the following suggestion. If one should succeed in devising an accumulator which can stand a very high temperature, and which has a considerable temperature coefficient of e. m. f. one might proceed in the following way. The accumulator is heated to a very high temperature, at which its e. m. f. may be relatively small, while it is higher at a low temperature. The cell might, therefore, be charged at high temperature produced by the burning of carbon. If it is then cooled, its e. m. f. increases, and the chemical energy is utilized at ordinary temperature.

For instance, Dolezalek has shown in his investigations on the lead accumulator that two accumulators filled with very dilute acid show a difference of e. m. f. of 0.6 volt, if there is a difference in their temperature of 90° C.

Similar conditions are found in galvanic cells with fused electrolytes which have been investigated by R. Lorenz and his co-workers. For instance, at 857° C. fused lead chloride may be decomposed at a tension of 1.08 volt into molten lead and gaseous chlorine; if the accumulator thus formed is cooled to 506° C. it has an e. m. f. of 1.28 volts. One might, therefore, use two such cells connected one against the other (i. e., lead connected with lead), one being hot, the other cold. Since the latter has a higher e. m. f., the current given out by it may be utilized for charging the hot battery, while the difference of 0.2 volt multiplied by the coulombs represents the heat which is transformed into electrical energy. It is self-evident that there is little hope to realize such cells for practical use, since heat conduction and radiation will cause a loss of energy in a similar way, as in the steam engine, so that the efficiency may be even lower than in the latter. Moreover, the melting point and boiling point of the substances used represent the limits of temperature within which the cell may be operated, so that no great difference of temperature is possible. It is therefore improbable that this scheme may ever find practical application.

To sum up, the carbon cell is theoretically possible and it seems certain that in future new points of view will be found for approaching the solution of the problem. On the other hand, it cannot be denied that, until the problem will be definitely solved, much is yet to be done, and many questions are to be solved which concern the difficulties involved in the internal resistance, polarization, self-discharge, influence of impurities, etc. The importance of the problem has attracted the interest of quite a number of men of science and engineering, and this fact justifies the hope that the thorough study of all questions which are concerned in the problem will lead to its final solution.

## FUEL AND HEAT BATTERIES.

By C. J. Reed.

In the newspapers and technical press two batteries representing attempts to get cheaper electrical energy from electrochemical reactions have recently been described, one of which was devised by H. Jone, the other by J. H. Reid. At the request of the editor of Electrochemical Industry, who has sent me descriptions* of these two batteries, I have written the following article.

The two batteries referred to do not appear to differ materially from other batteries which have been tried during the past twenty-five years.

In the Jone battery there is no attempt to get electrical energy from any reaction involving the oxidation of fuel. It is simply a galvanic battery of the ordinary alkaline type, in which metallic tin is substituted for metallic zinc. This is unusual, but not unheard of.

The additional apparatus, in which he conducts heat reactions for the purpose of regenerating exhausted material,

*The Jone battery is described in Electrochemical Industry, 1902, p. 586; the Reid battery in the present issue, p. 30.—Editor.

is no more a part of his battery than a zinc retort or furnace is a part of a gravity battery.

If a small zinc reducing furnace, operated in conjunction with, and as an adjunct to, a gravity battery for regenerating its waste material, would render the battery more economical as a source of energy than the same battery would be with zinc reduced on a large scale in zinc works, then we might reasonably expect a similar result from a tin battery. If such is the case, the evidence of it is not before us in the published description of the Jone battery.

According to this description metallic tin is converted into stannous oxide (SnO) and mercuric oxide (HgO) is reduced to metallic mercury, the reaction being represented

$$Sn + HgO = SnO + Hg$$

The theoretical electrogenic power of this reaction is 1.53 — 0.46 = 1.06 volts, and this is the electromotive force claimed by the inventor, but whether he obtained this electromotive force by calculation or by experiment is not stated. Assuming this to be the observed electromotive force on open circuit (which is all that the chemical reaction could supply), the greatest possible efficiency may be calculated from the other data supplied by Mr. Jone. He states that a cell holding 1.5 gallons of electrolytes gives 23 amperes through an external resistance of .02 ohm. The total resistance of a circuit through which 1.06 volts would produce a current of 23 amperes would be $\frac{1.06}{23} = 0.046$ ohm. As the external resistance is stated to be 0.02 ohm, the internal resistance must be 0.046 — 0.02 = 0.026 ohm, and the efficiency of the cell as an electric generator could not have exceeded $\frac{0.02}{0.046} = 43.5$ per cent.

The inventor states that the efficiency is 85 per cent, but the figures he gives shows that it could not have exceeded 43.5 per cent of the chemical energy of the reaction. To this loss of 56.5 per cent must be added the loss of all heat supplied and all energy used in operating the stiring and circulating apparatus and in recovering and regenerating the waste materials.

The effective output of the cell described could not have exceeded 1.06 x 23 x 0.435 = 10.6 watts. Mr. Jone does not state directly the density of the alkaline solution used, but it is reasonable to assume that it was not less than 1.25 sp. gr. This solution would weigh 19 lbs. and occupy 6.8 litres. In order to supply 1 hp-hour, this cell would have to be in operation 70.4 hours and would consume 14½ pounds of HgO and 8 lbs. of Sn, making the weight of the chemicals alone in this 1 hp-hour cell 41½ lbs. The output of the cell would be only 1-70 hp. The space occupied by the cell and furnace would certainly not be less than 3 and probably not less than 5 or 10 times that of the electrolyte, or roughly, from 3 to 5 cubic yards per horse-power of output. The space occupied by the regenerating apparatus described for regenerating nitric acid from nitrous fume, for reducing stannous oxide and for re-oxidizing the mercury, are not included, and this space would be enormous.

The reoxidation of the mercury to HgO by dissolving in nitric acid and driving off the nitric acid by heat is a process which Mr. Jone probably did not actually try, or he would not have recommended it. 1 hp-hour would require not less than 12¼ lbs. of absolute $HNO_3$ or 17½ lbs. of nitric acid of sp. gr. 1.422.

The recovery of the tin from 9 lbs. of stannous oxide, even according to the admission of Mr. Jone, would require from 1 to 1½ lbs. of coal and according to actual practice from 12 to 16 lbs. The loss of tin in the practical smelting of refined ore or "black tin" generally exceeds 10 per cent, and there is no reason to believe it would be less in the smelting of the stannous oxide residue from Mr. Jone's battery. This loss alone at the present price of tin would, in Mr. Jone's battery, amount to about 20 cents per horse-power-hour.

The recovery of 17½ lbs. of absolute nitric acid as nitrous fumes could be accomplished only by collecting it in many times its weight of water, all of which must be evaporated by heat. This alone would require 10 to 50 times as much coal as that required to produce 1 hp-hour in a steam engine.

Mr. Jone has evidently overlooked the enormous labor of collecting and handling the large quantities of bi-products, as well as the important fact that large mechanical losses are always inevitable in handling, smelting and refining large quantities of expensive materals, such as mercury and tin.

Mr. Jone assumes that his electrolyte of sodium hydrate undergoes no permanent deterioration. This assumption is contrary to all experience in batteries of this type and is not to be admitted.

It appears to the writer that the mere removal of stannous oxide from the cell and its separation from the electrolyte would cost for labor alone more than the coal would cost for producing the same amount of power by steam.

If we were to ignore losses of material altogether and consider only all the losses of energy occurring in the cycle of processes proposed by Mr. Jone, the cost of power would appear to be not less than 50 to 100 pounds of coal per horse-power-hour. A closer estimate cannot be made.

Mr. Jone seems to have realized the enormity of his undertaking and states that he has already discarded the mercuric oxide as a depolarizer and found another which is still a secret. What he may be able to do with this new depolarizer remains for him to demonstrate. We can only judge of what he has published.

The other battery referred to is that described in United States patents 736,016 and 736,017, issued to J. H. Reid. It consists essentially of an iron pot containing fused caustic soda, in which is immersed a porous carbon tube. The tube and iron pot are the electrodes. A current of illuminating gas is supplied to the surface of the electrolyte at its point of contact with the carbon tube.

Jablochkoff, Archereau, Jacques and many others have used the same battery without the fuel gas. Liebenow and Strasser in their experiments on this battery tried illuminating gas and found it did not give as good a result as air.

That the electrical energy of this cell is produced by thermo-electric action at the expense of heat and not by chemical energy has been shown elsewhere,* and may be seen by an inspection of the chemical reactions supposed to take place.

In all electrochemical reactions it must be borne in mind that the substances undergoing oxidation or other electrochemical change must actually transmit (conduct) the current corresponding to that electrochemical change. In terms of the theory of electrolytic dissociation this would be stated by saying that *the ions which change to atoms must do so by giving up electric charges to the electrodes and the atoms which change to ions must do so by receiving electric charges from the electrodes,* that is, by conducting the current.

It follows from this that a non-conducting gas, such as oxygen, hydrogen, marsh gas, and other fuel gases, cannot act as electrodes in a gaseous state. These gases, by merely coming in contact with an electrolyte or an electrode or both, would not become conductors and could not take part in an electrochemical reaction, any more than grains of sand or glass would become conductors by being dropped into an electrolyte. Non-conductors may, by *solution* in a liquid, become conductors and electrolytes. Before we can admit that fuel gases take part in an electrochemical reaction it must be shown that these gases are dissolved as conductors. In the case under consideration there is no evidence of such solution or conductivity.

Let us admit, merely for the purpose of working out a conclusion, that these fuel gases are dissolved and become conductors. The next question to be determined is the electromotive force they could produce in a reaction, and the amount

* See transactions of American Institute of Electrical Engineers, 1898.

of chemical energy which could be converted into electrical energy by their oxidation.

Electrochemical action can take place only by a chemical change in the molecules of an electrolyte through which the current passes in entering or leaving an electrode. If the gases in question are electrochemically oxidized at the anode, the oxygen must come from the electrolyte and must be derived from some oxide in the electrolyte. The only oxides present in the case under consideration are $H_2O$, $Na_2O$ and $Fe_2O_3$. The formation heats of these substances are

$$H_2O = 69{,}000$$
$$Na_2O = 155{,}900$$
$$Fe_2O_3 = 197{,}700$$

The formation heat of $CH_4$ is 20,414; of $CO_2$, 97,650; of CO, 29,400, and of FeO, 65,700.

The following equations represent the possible reactions which could take place in such a cell, oxidizing hydrogen, marsh gas, and carbon monoxide:

For Hydrogen.

$$2H + H_2O = H_2O + 2H \quad (1).$$
$$2H + Na_2O = H_2O = 2Na \quad (2).$$
$$6H + Fe_2O_3 = 3H_2O + 2Fe \quad (3).$$
$$2H + Fe_2O_3 = H_2O + 2FeO \quad (4).$$

For $CH_4$.

$$CH_4 + H_2O = CO + 6H \quad (5).$$
$$CH_4 + 2H_2O = CO_2 + 8H \quad (6).$$
$$CH_4 + Na_2O = CO + 2Na + 4H \quad (7).$$
$$CH_4 + 2Na_2O = CO_2 + 4Na + 4H \quad (8).$$
$$CH_4 + 4Na_2O = CO_2 + 8Na + 2H_2O \quad (9).$$
$$CH_4 + Fe_2O_3 = CO + 2Fe + 2H_2O \quad (10).$$
$$CH_4 + 3Fe_2O_3 = CO + 6FeO + 2H_2O \quad (11).$$
$$3CH_4 + 4Fe_2O_3 = 3CO_2 + 8Fe + 6H_2O \quad (12).$$
$$CH_4 + 3Fe_2O_3 = CO + 6FeO + 2H_2O \quad (13).$$

For CO.

$$CO + H_2O = 2H + CO_2 \quad (14).$$
$$CO + Na_2O = 2Na + CO_2 \quad (15).$$
$$3CO + Fe_2O_3 = 2Fe + 3CO_2 \quad (16).$$
$$CO + Fe_2O_3 = 2FeO + CO_2 \quad (17).$$

Of these reactions the first neither evolves nor absorbs energy, the original substances and products of the reaction being identical. All others, except 3, 4, 16 and 17, absorb energy, and consequently could not be sources of electrical energy. The electrogenic power of reaction 3 is only 0.07 volt, and the powers of 4, 16 and 17 are still less. The electromotive force of 0.9 volt per cell, which is claimed for this battery is, therefore, entirely or almost entirely thermo-electric.

## THE ELECTRICAL MANUFACTURE OF STEEL.

Process of Gustave Gin.

By P. McN. Bennie.

The following article is an abridged translation of M. Gustave Gin's description of his latest process for the production of steel by electrical means. The principle involved—that of heating a thin stream of metal by the passage of an electric current—is rather novel, and its originality justifies some notice of the process.

This method has been operated, the translator understands, only in an experimental way, thus far, and it therefore remains to be seen whether the calculations of the inventor can be realized in practice. Lacking such actual commercial operation, the translator wishes to disclaim any responsibility for such claims as may be advanced by M. Gin for this process.

It should be noted that the units mentioned are in the metric system, the ton referred to being equivalent to 2204 pounds avoirdupois.

General Considerations.

The changes in physical states and the reciprocal reactions of substances involved in the industrial production of iron and derived metals, require the consumption of a certain amount of energy, hitherto obtained by the combustion of carbon; in the present process an attempt is made to replace this by electrical energy.

The technical solution of this problem may now be considered an accomplished fact; but it is advisable to make certain reservations as regards the economic results. It must not be forgotten, in fact, that while electricity is the most tractable of the forms of energy, it is, generally speaking, also the most costly. It should not, therefore, be employed, except knowingly (with a thorough understanding of the conditions), and its use should be limited to those applications where its superiority is clearly evident. By carefully examining all the data of the problem, it appears certain that the application of electrical energy to the *direct extraction* of iron from its ores, cannot be advantageous, except under certain exceptional conditions.

Besides, it must be recognized that the modern blast furnace, to the perfecting of which so many metallurgists have concentrated their efforts, is a marvellous metallurgical instrument, in which the utilization of heat energy approaches so closely to perfection, that it is seeking Utopia to attempt to substitute for it the electrical furnace. Such a substitution is, furthermore, inconceivable, except in certain localities particularly favored as regards electrical energy and minerals.

But it becomes a different matter when electrical energy is used for the conversion of crude cast iron into steel. In this case the electric furnace clearly has the advantage of the Martin furnace, always providing that the electrical energy may be obtained at an acceptable price, either by the employment of hydraulic power for generating purposes, or by the use of the energy available in the waste gases from blast furnaces.

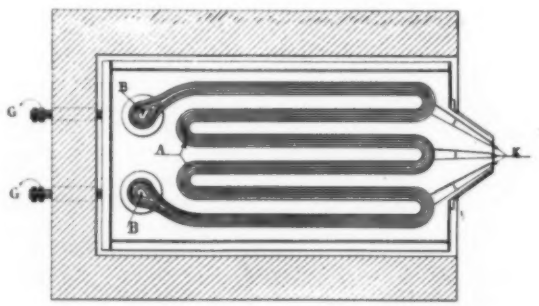


FIG. 1.—GIN STEEL FURNACE.

As soon as there is accomplished by the latter means the combination of the blast furnace for cast iron; the Bessemer converter for the common steels; and the electrical refinery for higher grade steels, the industrial metallurgy of iron will have realized an almost perfect utilization of the heat energy of coal.

Gin Process.

From the data submitted by Dr. H. Goldschmidt, of Essen, at the recent Fifth Congress of Applied Chemistry, at Berlin, it appears that the first electrical furnace for the manufacture of steel was proposed by M. Gin, in 1897 (1). Since that time researches upon this interesting question have been continued, and many new types of furnace for steel production have been studied. The latest type depends upon the utilization of the Joule effect, without the use of carbon electrodes.

In the various types of apparatus devised up to the present time, to produce electrothermic reactions in fused cast iron, great difficulties have been experienced in utilizing the energy of the electric current in a bath, the resistivity of which scarcely exceeds 200 microhms per cubic centimeter; generally one is content to produce the Joule effect in a layer of slag

(1) French Patent No. 263,783—February 6, 1897.

floating on the metallic bath, using the notably higher resistivity of this slag.

Besides, the use of carbon electrodes is an obstacle to decarborization, because reduction of the constituents of the slag is effected by the carbon of the electrodes, rather than by the combined or dissolved carbon in the bath.

Finally, furnaces have been devised where the current which passes through the bath is generated by induction, and without the use of any electrodes. But it should be noted that such an apparatus is costly, and involves a considerable magnetic

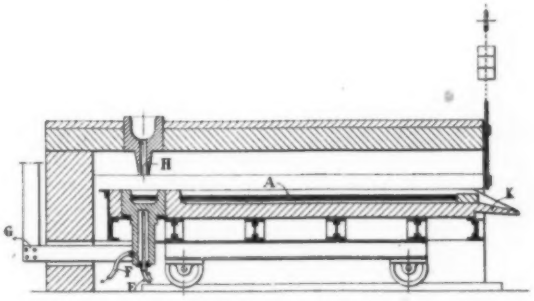


FIG. 2.—GIN STEEL FURNACE.

leakage, incompatible with an efficient utilization of electrical energy.

For the purpose of avoiding these undesirable features, the expedient of the slag bath, and the objectionable use of carbon electrodes, the idea arose of forming the electric furnace as a canal or channel of great length, and small cross section; filling this canal with fused cast iron; and having at its terminals blocks of steel cooled by an internal current of water.

The passage of the proper amount of current in the conductor of fused metal sets free a sufficient quantity of heat to maintain the whole mass in fusion, and to bring it to the most favorable temperature for producing the refining reactions. On the other hand, the large section of the blocks forming the terminals of the circuit prevents a great rise of temperature in them, being aided in this respect by the circulation of cold water.

To give a convenient form to the hearth, the canal in which the metal is held is doubled on itself several times, so that there

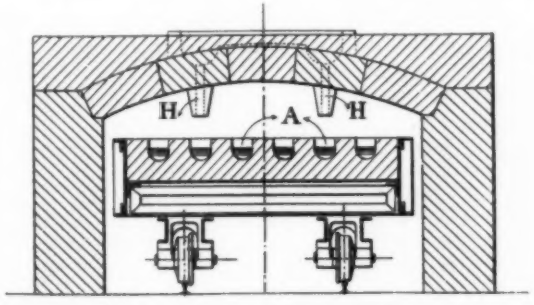


FIG. 3.—GIN STEEL FURNACE.

is formed a sort of huge incandescent lamp, of which the filament consists of a stream of molten iron.

In practice the apparatus would consist of a movable carriage on rails, having a body made of refractory materials. In this carriage body is placed the hearth, containing a channer or canal, having rectangular and semi-circular cross-section (A), and sinuous in a longitudinal sense. The ends of the canal connect with the terminals for the current supply (BB), each of these consisting of a block of steel so shaped as to form an open basin in the canal. The terminal blocks carry a vertical downward extension, which serves for the connection (G), with the conductors carrying the current. These terminal blocks are cooled by an interior circulation of water, which is introduced into the cavity (D) by means of the tube (E), connected with a reservoir by means of a strong rubber tube; the water escapes by the orifice (F), which is also connected by rubber hose to the sewer.

When a charge of metal is to be refined, the crucible carriage is placed in an arched furnace, in order to reduce as much as possible loss of heat by radiation. The furnace being in place, electrical connection is made at (G), and the fused pig-iron is introduced by the funnels (H).

The dilution method (scrap process) may be employed by adding to the iron a calculated proportion of scrap iron, which dissolves in the fused bath. The carbon of the iron diffuses with great rapidity throughout the mass, and the conversion of the whole into steel takes but very little more time than that needed for the fusion of the added metal.

It is also easy to employ the method of oxidation, by the addition of some iron oxide (ore process). The oxygen of the iron oxide added to the bath burns the silicon, manganese and carbon. As in a furnace of this type the temperature can be elevated at will, the carbon is eliminated with great

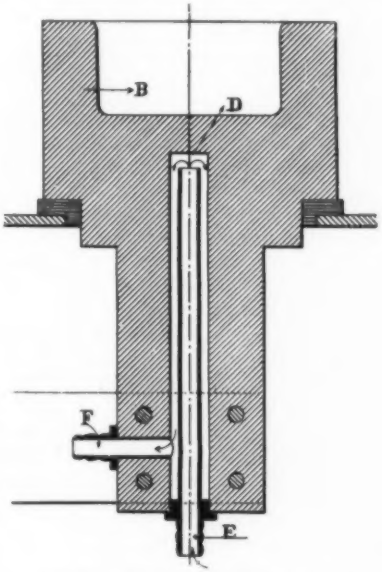


FIG. 4.—GIN STEEL FURNACE.

rapidity, thus obtaining a more complete dissociation of the iron and carbon of the pig iron.

When the pig iron, or mixture of pig iron and scrap, has become well fused, the iron oxide is added by means of a shovel; quite a lively ebullition is produced which lessens gradually. When the process of decarbonization is only manifested by the small blue flames which escape periodically at the surface of the bath, a further quantity of oxide is added. The same phenomenon occurs, but not so strongly marked this time, and the extent of decarbonization is judged by the feebleness of the blue flames.

At this time the test specimens may be taken, and, if necessary, the final additions of spiegel or ferro-manganese may be made, although these latter are not so important in this as in other types of furnaces; this is particularly true with reference to the silicon generally employed to play the rôle of intermolecular combustible, this being quite unnecessary with electrical heating of the metal.

It is interesting to note that in this electric furnace the oxidation of the impurities of the pig iron, and notably that of the carbon, is brought about without the intervention of atmospheric oxygen. Thus the amount of dissolved oxide is reduced, and, consequently, the quantity of deoxidizing ma-

terials to be introduced at the end of the operation is lessened.

It should be remarked that the localization of the heating in the metallic conductor, enables one to obtain temperatures which would not be realizable in furnaces of the Martin type, without melting the arches, and consequent danger of spoiling the metal exposed on the hearth.

The dephosphorizing and desulphurizing materials may be introduced at practically any moment after the metal is well fused; either before, or during, or after the decarbonization. The removal of the slag is effected by means of an iron scraper, which is manipulated by the workmen from the front of the furnace.

The finished metal is poured at the openings (K), which are placed at the front, or end of the furnace opposite the electrical connections.

The method by oxidation (ore process) is dwelt upon at some length, and less has been said about the method by dilution (scrap process) on account of the considerable modifications that would be necessary in the section of the bath, and the necessity which it would entail of varying the voltage of the electric current between wide limits.

The dilution method only possesses real interest in the case of a factory exceptionally placed with reference to a supply of pig iron containing but little sulphur or phosphorus. In fact, it should be kept in mind that dilution without simultaneous oxidation would require the use of very pure materials, because the elimination of impurities would be insignificant.

All the advantages of these two methods may be combined, and their respective inconveniences avoided, by the use of a "mixed method," involving the use of a certain amount of scrap, and oxidation by the addition of iron oxide. It should be noted, moreover, that even in the Martin furnace, the "ore process" is not rigorously followed, but that about one-fifth of the total charge is scrap iron.

The following shows the manner in which it is proposed to operate the Gin furnace in practice:

The pig iron is treated with some iron ore and lime, so as to oxidize the impurities, while producing a basic slag, which facilitates the elimination of the phosphorus. When the purification is sufficient, the scrap iron is introduced into the very hot bath, the slag is removed when fusion is complete, and the final additions of ferro-manganese are made, to reduce the oxide dissolved in the metal.

It is understood, of course, that the use of this mixed process is dependent upon the nature of the possible supply of raw materials; but it is especially adapted for those factories which can obtain at good prices scrap iron, rail ends, bars, sheets, etc., suitable for making proper mixes.

### Special Steels.

It is believed that this type of furnace will permit of the easy manufacture of special steels, by the direct incorporation of the additional elements—manganese, nickel, tungsten, vanadium, molybden, etc. Special grades, having a high manganese content, and containing but very little carbon, may be obtained by adding to the bath a suitable proportion of silicon-manganese (which was first prepared by M. Gin, by reduction of rhodonite—French patent No. 316,111), and by oxidizing the silicon by means of manganese dioxide, according to the reaction:

$$mFe + 2nSiMn_2 + 3nMnO_2 = \underset{\text{Metallic bath}}{mFe + 5nMn} + \underset{\text{Manganese steel}}{} \quad \underset{\text{Slag}}{+2nMnSiO_4}$$

It is desirable in this case not to push the temperature of the bath too high, because the manganese is eliminated spontaneously by vaporization.

### Furnace Materials.

The materials of which the hearth of the furnace is constructed should obviously be sufficiently refractory to withstand the highest temperatures of the bath. Under this head, lime and magnesia would be preferable, if these bodies were not so easily converted into slag by the silica resulting from the oxidation of the silicon in the bath.

It is true that lime and dolomite play an important part as dephosphorizing and desulphurizing agents, but it is better to employ the calcareous materials mixed with the oxidizing agents. As for silicious linings, they are not sufficiently infusible to be used without rapid deterioration. The best protective coatings are found in rich bauxite, and above all in chromite of iron, which may be agglomerated by ordinary methods.

### Example of Application of Process by Oxidation.

For an iron containing:

| | |
|---|---|
| Carbon | 3.60 per cent. |
| Silicon | 1.68 " " |
| Manganese | 1.10 " " |
| Phosphorus | 0.62 " " |

The proportions of the above impurities have been chosen arbitrarily to facilitate calculation. The composition of a ton of pig iron may, in fact, be represented by the simple formula here given, expressed in kilogram-molecules:

$$16.6Fe + 3C + 0.6\ Si + 0.2\ Mn + 0.2\ P\ldots.$$

If we suppose that the finished steel contains 0.96 per cent carbon, and 0.28 per cent silicon; and if we admit for the simplifiaction of the formulas, that the other impurities are practically eliminated, the ensemble of the reactions may be reduced to the equation:

$$x(16.6Fe + 3C + 0.6Si + 0.2Mn + 0.2P..) + yFe_2O_3 + zCaO$$

$$= \underset{\text{One ton of steel.}}{17.7Fe + 0.8C + 0.1Si} + \underset{\text{Carbon monoxide disengaged.}}{(3x - 0.8)\ CO}$$

$$+ x(0.5SiO_2 + 0.2MnO + 0.6CaO + 0.6FeO) + 0.1x(P_2O_5 4CaO)$$

Pig iron. Ore. Lime.

Slag.

From this it follows that the production of a ton of steel requires:

| | |
|---|---|
| Pig iron | 919 kilogr. |
| $Fe_2O_3$ | 218 " |
| CaO | 56 " |

The quantities eliminated theoretically amount to 57.6 kg., while there is a recovery of 134.8 kg. of iron. We may admit, as practical, the following figures for the production of one ton of steel, by the method of oxidation:

| | |
|---|---|
| Consumption of pig iron | 924 kg. |
| Iron ores (75 per cent $Fe_2O_3$) | 320 kg. |
| Lime | 56 kg. |

### Energy Consumed.

The calorific energy derived from the electric current is utilized as follows:

a Heating the metallic bath from 1300° to 1750° C.,
b Heating the reagents to 1600° C.,
c Chemical reactions,
d Radiation losses.

a——Heating the metallic bath:

We raise the temperature of 924 kg. of iron from 1300° to 1750°. But, between these two temperatures the specific heat of the iron varies between 0.40 and 0.58 (which gives 0.48 as mean value). The heat consumed is therefore:

$$q_a = 924 \times 0.48 \times 450 = 199{,}600 \text{ calories.}$$

b——Heating the reagents:

The specific heats (average) of $Fe_2O_3$ and CaO between 0° and 1600° C. are respectively 0.19 and 0.23, so that the heat consumed in heating the reagents is:

$$q_b = (320 \times 0.19 + 60 \times 0.23) \times 1600 = 119{,}400 \text{ cals.}$$

c——Chemical reactions:

By balancing the heats of formation of the compounds which occur in the two members of the above equation, we have:

$q_a = 75{,}000$ calories.

The total of the calories expended for the heating of the masses, and the chemical reactions is therefore:

199,600 + 119,400 + 75,000 = 394,000 calories,

which corresponds to a consumption of 456,000 watt hours per ton of steel manufactrued.

d——Radiation losses:

The masonry of the furnace structure being heated by preceding operations, the iron destined for the next operation is introduced at a temperature which does not materially exceed that of the interior of the furnace. The calorific emission of the bath is, therefore, of but minor importance at the beginning, but it increases as an exponential function of the heating of the metal, which is at first very rapid, when nearly all the heat generated by the current is used in heating.

To reduce these losses, when the temperature of the bath reaches 1500° C., it is covered with some of the ore and lime.

At the very first these reagents are heated as much by radiation from the furnace interior as by contact with the bath, of which the radiation is momentarily almost annuled. When the reagents have been converted into slag and fused, radiation occurs at the surface of the liquid slag; later, when the purifying reactions have terminated, the slag is cleaned off, and the surface of the bath being exposed, radiation becomes intense, the temperature finally tending to reach a point where there is a balance between the generated and dissipated heat.

From a few experiments which were made, it has been concluded that the emission of heat from a carefully installed furnace may be expressed provisionally by the following formula, derived from that of Stephan:

(1) $$w = aST^4\theta$$

where

$w$ = the dissipated energy expressed in watt hours,

$a = 3125 \times 10^{-18}$,

$S$ = radiating surface of the bath of steel = lc (l and c being the length and upper surface of the metallic stream),

$T$ = temperature (maximum absolute) = 2000° C.

$\theta$ = time in hours.

From the above it follows that

(2) $$w = 5lc\,\theta$$

### TOTAL EXPENDITURE OF ENERGY.

For a furnace of power W, producing P kilograms of steel per operation, during $\theta$ hours, the calorific expenditure would be equal to

(3) $$W\theta = 456P + 5lc\theta$$

### DATA OF CONSTRUCTION AND YIELD OF FURNACES.

The preceding formulæ may be represented under another form. Admitting that the density of the liquid iron equals 7, we have:

(4) $$7lc^2 = 1000\,P$$

or

(5) $$lc^2 = \frac{1000\,P}{7}$$

It may also be noted that at any given moment, we have:

(6) $$W = \frac{E^2}{R} = \frac{E^2c^2}{Pl}$$

In order not to introduce new variables, suppose that the moment of commencing a furnace run is the precise instant chosen for the verification of the preceding equation. At this moment we know approximately the value of $P = 216 \times 10^{-8}$, and we will assume that $E = 15$ volts. We therefore evolve from (6) the following equation:

(7) $$\frac{l}{c^3} = \frac{104 \times 10^4}{W}$$

From the equations (6) and (7) we deduce:

(8) $$l = 122000 \sqrt{\frac{P}{W}}$$

(9) $$C = 0.108 \sqrt[4]{PW}$$

(10) $$lc = 1318 \sqrt{\frac{P^3}{W}}$$

This latter value, substituted in equation (3) gives:

(11) $$W\theta = P\left(456 + 6590\,\theta \sqrt[4]{\frac{1}{PW}}\right)$$

Admitting that a single operation will occupy three hours, the time necessary for the reactions, we may show, by means of equation (11) the following curves, for the values of l, c and P, as a function of W:

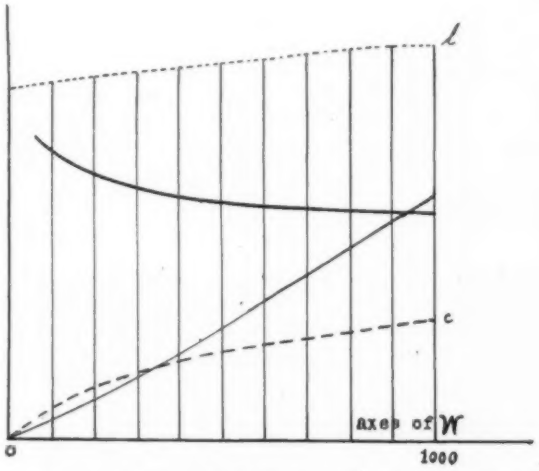


FIG. 5.—CURVE *l* (SCALE 1/100), CURVE *c* (SCALE 1/10), THE THIN, DRAWN OUT CURVE GIVES THE WEIGHT OF METAL PER OPERATION; THE THICKER CURVE THE EXPENDITURE OF ENERGY PER TON

### APPLICATION OF THE MIXED PROCESS.

Again taking up the figures of the preceding application (oxidation process), we may write the equation which symbolizes the ensemble of the reactions, thus:

$$x(16.6Fe + 3C + 0.6Si + 0.2P + \ldots) + yFe_2O_3 + zCaO + uFe$$

$$= \underbrace{(17.7Fe + 0.8C + 0.1Si)}_{\text{Pig iron}} + \underbrace{(3x - 0.8)\,CO}_{\text{Carbon monoxide disengaged}} + \underbrace{x(0.5SiO_2 + 0.2MnO + 0.6CaO + 0.6FeO + 0.1P_2O_5 + 0.4\,CaO)}_{\text{Slag}}$$

Ore, Lime, Scrap; Finished steel

Taking, for instance, x as being equal to ⅞, we deduce from the preceeding equation the following proportions as corresponding to the production of one ton of steel:

| | Theory. | Practice. |
|---|---|---|
| Pig iron ..... | 667 kg., | 670 kg. |
| $Fe_2O_3$ ..... | 145.70 kg., | 210 kg. (75 per cent) |
| Lime ..... | 40.90 kg., | 45 kg. |
| Scrap ..... | 267.68 kg., | 285 kg. |

Consumption of energy:

a——Heating bath of pig iron,

$q_a = 670 \times 0.48 \times 450 = 144{,}700$ calories,

b——Heating the reagents,

$q = (210 \times 0.19 + 45 \times 0.23) \times 1600 = 80{,}400$ cals.

c——Chemical reactions,

$q = 48{,}900$ calories.

d——Fusion and heating of the iron,

$q_4 = 285\ (410 + 0.48 \times 240) = 149{,}700$ calories.

c——Radiation losses,

$q_c = 5\ lc\theta$ watt hours.

For a furnace of W kilowatts, producing P kilograms of steel for each run of $\theta$ hours, we have:

(12) $$W\theta = 480P + 5\ lc\theta$$

By taking the same calculations as the preceding case we have:

(13) $$l = 1220 \sqrt[4]{\frac{P}{W}}$$

(14) $$c = 0.53 \sqrt[4]{PW}$$

(15) $$lc = 1863 \sqrt[4]{\frac{P^3}{W}}$$

(16) $$W\theta = 480\,P + 9315 \sqrt[4]{\frac{P^3}{W}}$$

By taking the value of $\theta = 3$, the equation may now be written:

(17) $$W = P\left(160 \times 9315 \sqrt[4]{\frac{1}{PW}}\right)$$

From these equations we may construct the following curves:

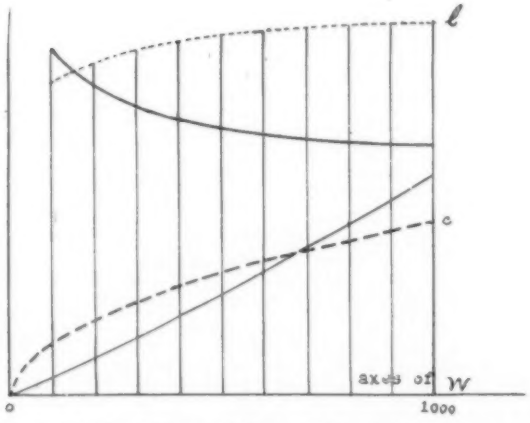


FIG. 6.—THE DOTTED CURVES REPRESENT $l$ AND $c$, THE THIN, DRAWN-OUT CURVE THE WEIGHT OF METAL PER OPERATION; THE THICK CURVE THE EXPENDITURE OF ENERGY PER TON.

### Cost of Production of Electric Steel.

In order to determine the cost of production of the steel, we will suppose that the electrical furnaces receive the pig iron direct from the blast furnace. These calculations have been based upon an annual production of 30,000 tons of 2204 pounds each:

| | Ore process. | Mixed process. |
|---|---|---|
| Pig iron | 925 kg.. | 670 kg. |
| Scrap iron | ... | 285 kg. |
| Iron ore (75 per cent) | 320 kg.. | 210 kg. |
| Lime | 56 kg.. | 45 kg. |

Following the preceding calculations, and supposing electric furnaces of 650 kw., there would be expended:

| | Ore Process | Mixed Process. |
|---|---|---|
| Electric furnace (30,000 tons) | 16,200,000 kw-h | 18,000,000 kw-h |
| Machinery and appliances | 2,640,000 kw-h | 2,400,000 kw-h |
| Total | 18,840,000 kw-h | 20,400,000 kw-h |
| For 8000 hours annual operations | 2,355 kw | 2,550 kw |
| Or, allowing for losses and hindrances of all sorts | 2,400 kw | 3,700 kw |

(Note): Here follows a series of calculations showing the cost of materials, labor, operation, etc., which, being based upon French prices, would not give an accurate idea of cost for America. As a result, it is claimed that steel can be produced from pig iron at about 83 francs (about $16.60) per ton of 2204 pounds avoirdupois.—*Translator.*

### Conclusions.

In order to avoid the accusation of undue optimism, the preceding estimates, it is claimed, have been based upon prices sufficiently high, and the electrical energy can easily be had at the price calculated ($16.00 per kilowatt year). (This is quite true in France.—*Translator.*)

A combination of conditions more favorable would reduce still further the cost of production. It is not difficult to imagine a company having minerals at $2.60 per ton, and proprietor of hydraulic power. Under such circumstances the electrical energy would be available at $8.00 per year per kilowatt, which would still further reduce the cost per ton of finished steel.

The translator desires to add that some water powers can be rented at as low as $8.00 per kilowatt year; such powers would supply current up to 5,000 kw. at least.

The idea certainly contains some food for reflection, and, as pointed out by the translator in a previous article,* would warrant careful study upon the part of our American blast furnace operators.

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## EXTRACTING GOLD AND SILVER AT WALLSTREET MILLS, COLORADO.

By Frank C. Perkins.

An electro-chlorination process has recently been developed by Mr. John E. Greenawalt, and is now in continuous operation at Wallstreet, Col., in the mill of the Nancy G. M. & T. Co. The accompanying illustration Fig. 1, is an exterior view of this mill, which is located about a third of a mile from the mine. The ore is first crushed and is sampled, one ton in twenty, being taken to the sampling room automatically, as the ore leaves the crusher and passes to the elevator, which carries it to the ore bins and dryers. After it has been completely dried, it is automatically fed to several sets of Davis rolls, which thoroughly pulverize the ore. It then passes to another large ore bin, and is ready for the furnace. The ore is conveyed to the roasting furnace, which is heated by means of

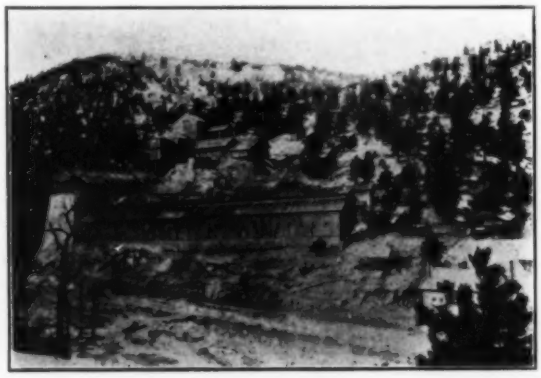


FIG. 1.—WALLSTREET MILL, COLORADO.

two Greenawalt gas producers, utilizing bituminous coal. On leaving the roasting furnace the ore drops into a furnace pit, where salt is added to chlorinize the silver, and some of the baser metals, which would consume chlorine in the vats, were the salt not added. The accompanying illustration, Fig. 2, shows the large leaching vats, to which the ore is conveyed

*Electrochemical Industry, 1902, p. 165.

after it leaves the furnace pit, and Fig. 3 shows the arrangement of the regenerating cells, in which the chloride and bromide solution is converted into an active gold solvent. The illustration, Fig. 4, shows the precipitating tanks where the metals are precipitated by the action of the electric current, the gold and silver being deposited from the solution.

### THE CRUSHER AND SAMPLER.

The Wallstreet mill is equipped with a 16 x 24 Blake rock

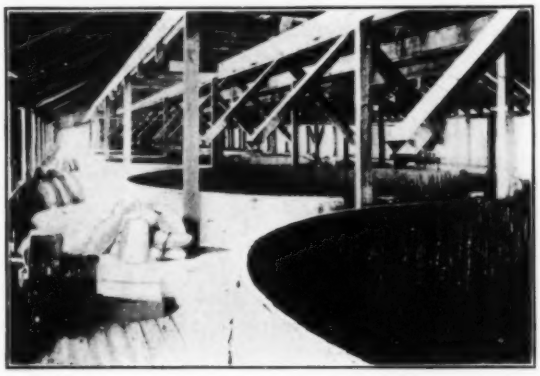


FIG. 2.—LEACHING VATS.

crusher, and, as above mentioned, the ore is automatically sampled as it passes to two large ore bins and dryers. The ore is very refractory, containing telluride and sulphide minerals, with an average of about 8 per cent sulphur. The ore conveyed to the sampling room is rolled to 3-inch mesh, and again sampled and ground.

### DRYERS AND ORE BINS.

The dryers, as well as the ore bins, are of special construction, and are of more than passing interest. There is an outer cylinder bin 40 feet high, and 12 feet in diameter, constructed of sheet steel, and another inner steel shell also of cylindrical shape, with its top covered. The inner shell is 15 feet high, and 7 feet in diameter, and this leaves a space of about 2½ feet for the ore between the two cylinders. There are a large number of 1-inch holes in the inner as well as the outer cylinders, and the waste gases from the boilers are forced through these holes in the inner cylinder, finally passing

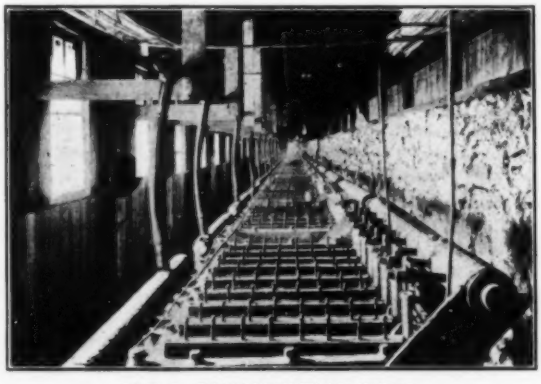


FIG. 3.—REGENERATING CELLS.

through the two or three feet of ore. The heat from these waste gases dries the ore thoroughly, when it is ready for the rolls.

### THE PULVERIZING ROLLS.

The mill is equipped with several sets of 16 x 42-inch Davis pulverizing rolls, and the ore is automatically taken from the bins above mentioned, and fed in even and constant streams through the rolls, which pulverize it to a 12 mesh. It will be noted that the ore, in being dried by the waste gases, saves a heavy expense for fuel and labor. The storage bins, which hold the ore as it passes to the rolls, have each a capacity of 500,000 pounds, or a total of several hundred tons. The roll room is also equipped with Jeffrey inclined vibrating screens, and continuous bucket elevators operated at slow speed. The ore, after being pulverized in the roll room, passes to another large ore bin, with a capacity of 1,000,000 pounds of crushed ore, which is ready for the roasting furnace.

### THE ROASTING FURNACE AND GAS PRODUCERS.

The ore is fed to the furnace in an interesting manner, adjustable gates being provided at the front of the ore bin, and the ore rushes out through the openings of these gates, while rabble plows cut into and plow the ore to the hearth of the furnace. It will be readily seen that the amount of ore which is fed to the furnace can easily be controlled by lowering or raising the bin gates above referred to. The two gas producers designed by John E. Greenawalt, use pea coal, which is converted into ashes and producer gas. These gas producers have fuel beds, somewhat less than 4 feet in depth, supported on a water-sealed bed of ashes. The coal is fed to the gasifying zone continuously and automatically, while the steam and air passes through the white-hot fuel bed, thus forming the producer gas. The gas burns between the ore bed and the arch, and the flame of gas can be thrown throughout the entire length of the roasting furnace. This furnace has a straight

FIG. 4.—PRECIPITATING TANKS.

line reverberatory with a roasting hearth 120 feet in lenght, and somewhat less than 12 feet in width. There is an endless chain at each side of the furnace, to which the ends of the rabbles are attached. The endless chains pass over sprocket wheels at one end of the furnace, and over sheave wheels at the other end. Ball bearings are provided for the rabble wheels, which run on a hollow cast-iron track on each side of the furnace, which is kept cool by a water pipe passing through it. This furnace has been found to give excellent satisfaction, with little or no trouble in connection with the passing of the rabble and chains directly through the furnace.

### THE FURNACE PIT.

The furnace pit is capable of holding 300,000 pounds of red-hot roasted ore, which drops into the pit as it passes through the furnace. The pit is 12 feet in diameter, and, as mentioned above, a small amount of salt is added as the ore falls into this pit. The ore is continually withdrawn from the lower portion of the pit, and the ore is cooled as it nears the bottom, where it is taken out, the red-hot ore, of course, being at the top, cooling and digesting in its own heat, on the way down for about twenty-four hours, when it is ready to be conveyed to the large leaching vats.

### THE LEACHING VATS.

The leaching vats are constructed of wood, as shown in Fig. 2, and are about 5 feet deep, and 30 feet in diameter. At

the bottom of the vats, sand is used as a filter, and they are constructed similar to leaching plants for cyanide solutions. The solution employed in these leaching vats is a strong brine, the solution of common salt being about 15 per cent. The solution also contains bromine, about ⅛ per cent, in the form of a bromide.

### The Regenerating Cells.

The regenerating cells consist of a series of two compartments, the cathode department and the anode compartment, the two being separated by means of an asbestos mill board porous diaphragm. Two perforated wooden boards on each side of this asbestos diaphragm are used to support it and hold it in position. A series of graphitized carbon plates are used as anodes, these carbon plates measuring ⅝ x 20 x 4. A sheet of perforated lead is used as cathode. The solution, as it passes through the regenerating cells from the leaching vats and precipitating cells, is charged with free bromine and chlorine, and compounds of these two elements, by the action of the electric current. Thus the chloride and bromide solution is converted into an active solvent of gold, and it dissolves the gold and silver as it percolates through the ore into large vats, and then passes through a series of precipitating tanks, where the metals are deposited by the action of the electric current. The solution passes again through the regenerating cells, where it is again charged with chlorine, and again passes through the ore. In this way the solution is used over and over again continuously. In the regenerating cells in passing through the solution, the current electrolyzes the sodium chloride, and this takes place with the evolution of hydrogen and formation of sodium hydroxide at the cathode, while chlorine gas and compounds are produced at the carbon anode and are absorbed by the solution until it is thoroughly saturated; then bromine or chlorine gas is released. This gas is collected and brought into contact with the ore, which is in the furnace pit.

In the regenerating cells the current density is about 20 amperes per square foot, a current of about 400 amperes being received by each cell, the potential being about 4¼ volts. Mr. Greenawalt states that 12 of these cells are sufficient to treat 200,000 pounds of ore, when the latter is free from alkaline compounds or lime, and is thoroughly roasted. He states that the object sought is to saturate the solution around the carbon plates with chlorine, and then pass it to the ore. The solution is thus made a medium of transporting chlorine to the ore mass.

### The Precipitating Cells.

The cells in the precipitating room, seen in Fig. 4, are filled with lead plates, arranged about 1½ inches apart, one-half of the plates being connected with the negative conductor, and one-half to the positive. The solution passes around these plates in a zigzag path, the gold and silver being deposited upon the cathode plates. This deposit is in the form of a slimy black powder, a large proportion of it dropping to the bottom of the tank. In the precipitating cells the current density is 1/36 ampere per square foot. Mr. Greenawalt states that by extracting the silver with the gold it is possible to treat gold-silver ores to a much higher percentage than by other methods. In order to extract the silver, chloride of silver must be formed in the furnace pit and the strong solution dissolves this silver chloride, the free chlorine acting upon the gold contents of the ore. The Greenawalt electro-chlorination process is being introduced by the Wallstreet Gold Extraction Co., of Wallstreet, Boulder County, Col.

# SYNOPSIS OF ARTICLES IN OTHER JOURNALS.

*A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.*

### Industrial Electrochemistry.

*Electrolytic Refining of Gold.*—With reference to the paper of Tuttle, published in Electrochemical Industry, 1903, page 157, on the Wohlwill process used in the Philadelphia mint for the electrolytic refining of gold, the inventor of the process, Wohlwill, makes some remarks in *Zeit. f. Elektrochemie*, October 29. In the Philadelphia mint no bullion is treated which has a fineness less than 0.940 gold, so that it contains never more than 5 per cent of silver. The present author states that this is not necessarily a supposition for the application of his process, but is rather due to the fact that in Philadelphia a temperature of 50° to 55° C. is used, which is 15° to 20° below what he considers to be the normal temperature for his process. This relatively low temperature is said to have considerable influence, not only on the properties of the deposited gold, but also on the solution of the anode. The cathodic gold deposit obtained in Philadelphia is soft, and under slight pressure it may be formed in a die press, while the gold deposited at the higher normal temperature is compact and coherent and cannot be formed by slight pressure. On the other hand, at the normal temperature a larger anodic current density may be used than with the temperature 10° or 15° lower, without developing chlorine at the anode. The use of a lower temperature requires, therefore, a lower current density. If the normal temperature is used and no special haste is necessary, even the most impure Klondike gold, containing 21.9 per cent of silver, may be refined by the Wohlwill process. If one wants, however, to refine the main part of the gold in twenty-four hours, the contents of silver should not be more than 15 per cent, even at the normal temperature. Alloys with a content of silver of approximately this amount are continually refined in Hamburg. If the content of silver is 8 or more per cent, it is necessary to scrape off, from time to time, the layer of silver chloride formed on the anode.

*Treatment of Slimes by Cyaniding and Electrical Precipitation on a Mercury Cathode.*—In a paper by Mumford, published in the *Transactions Australas. Inst. Min. Eng.*, 1903, 9, page 96, and abstracted in the *Journal of the Society of Chemical Industry*, September 15, the advantages for the electrolytic precipitation of gold on a mercury cathode are summed up as follows. Extraction and precipitation may be effected without filtration; the solution need not be clear for precipitation; the precipitation is equally good, whether from strong or very weak cyanide solutions; the presence of copper salts is not detrimental; the gold is recovered as an amalgam, which only requires retorting and melting; amalgamation of slimes beforehand is unnecessary, as any coarse gold present is amalgamated during precipitation. The essential features of a mercury cathode are thus summarized: The surface of the mercury should be as large as possible, and be kept in perfect condition by some simple means; the minimum quantity of mercury should be used; and the right current density should be employed. Some information is given on the Riecken process and the Mumford process. The Riecken process has been employed at the South Kalgurli mine since December, 1900, about 3,000 tons per month being now treated. In this process an iron vat is used with vertical ends, 11 feet high, by 8 feet wide, with inclined sides 13 feet long, and rounded bottom. It holds 17 tons of ore. Paddles mounted on a horizontal shaft passing through stuffing boxes at the ends are rotated at 12 revolutions per minute. The sides and bottom form the cathode, and are lined with amalgamated copper, over which mercury is kept flowing, being drawn off below and elevated by compressed air to the top of the vat. Iron bars, 3 inches by

1 inch, suspended about 18 inches from the bottom, serve as anodes. The discharge valve for the pulp is placed 4 inches from the bottom, and the mercury remains in the vat during the discharging period. About 400 to 500 pounds of mercury are required for one vat.

MUMFORD'S electro-cylinder consists of a steel plate cylinder, lined with amalgamated copper, and with wooden ends; it is supported on rollers and rotated at 5 revolutions per minute. The anodes are 2-inch round iron bars, supported from end to end of the cylinder, and making electrical contact by means of brushes outside the cylinder at one end. Wooden bars to assist the agitation are similarly supported. A 6-inch valve, with an elbow, is placed at one end, 3 inches from the bottom, for use as a discharge in that position, or as an inlet when the cylinder is turned through a half revolution. A spring valve for the escape of gases is also provided, opened automatically by a tappet, when it is at its highest point. A locked mercury cock is placed in the periphery of the cylinder. In use, mercury is charged in until it is ½ inch deep on the bottom, and the cylinder is filled with charge within a few inches of the top. The whole is then rotated on its horizontal axis at 5 revolutions per minute, and current is supplied at a density of 0.5 amperes per square foot of the amalgamated copper cathode surface. The latter is kept clean by its frequent plunge beneath the mercury bath. Most of the amalgam passes into the mercury, and can thus be run off at the "clean-up." Amalgam adhering to the copper is removed by returning the cleaned mercury and agitating it with sand, if necessary, after softening the amalgam by means of steam. A cylinder 20 feet long and 5 feet in diameter holds 16 tons of pulp (equal weights of solution and ore), and requires about 300 pounds of mercury and 150 amperes. A slime assaying 6 dwts. of gold would require about eight hours for complete precipitation, or one assaying 1 to 2 ounces about 12 to 16 hours. Prior to use, battery tailings would be classified to separate sand, and the slimes would be thickened to the right consistency in spitzkasten; they would then be transferred to agitation vats and mixed with cyanide. By modifications described the process is applicable to sulpho-telluride ores. The current density to be employed depends largely upon the condition of the surface of the mercury. When the cylinder was maintained in rotation a current density of 0.8 ampere per square foot could be used as a maximum, but any higher density led to a partial surface-deposit of gold, which did not amalgamate, and which was mechanically retained in the pulp. At 2 amperes per square foot, none of the deposited gold amalgamated, but all was lost. Rose has fixed 0.01 ampere per square foot as the maximum for simultaneous precipitation and amalgamation, this low figure being probably accounted for by the difficulty of keeping the mercury surface in good order. With weak solutions it was found that the weight of gold deposited was not in proportion to the current density, and a current density of 0.5 ampere was practically as good as one of 0.8 ampere per square foot. The potential difference may be from 3 to 5 volts. It is recommended to add salt if fresh water be used.

*Electric Smelting of Copper.*—In a paper, published in the *Mémoires de la Société des Ingenieurs Civils de France* and abstracted in *Engin. Mag.*, November, VATTIER gives an account of tests made at Grenoble with the Keller and Leleux furnace for the electric smelting of copper. The tests were made with samples of Chilean copper ore and 8,000 kg. of ore were treated in the electric furnace and fully reduced to a matte in eight hours by the expenditure of 500 kw. The ore contained about 7 per cent of metallic copper, and the resulting matte showed 43 per cent of metallic copper, while 0.1 per cent of copper was found in the slag. The consumption of the carbon electrodes during the operation amounted to 6 to 7 kg. per ton of ore treated, but by the use of artificial graphite electrodes this consumption may be reduced to 5 kg. per ton. The furnace used is of the double type, there being an upper crucible in which the ore is fused in the arc formed between two electrodes, and a lower portion into which the fused material flows, the latter being provided with movable carbon electrodes, which may be plunged into the molten bath, or raised above the surface. By this arrangement the fusion is effected in the first crucible, and the reduction in the second one, the latter operation being capable of close regulation, the slag being drawn off above, and the fused matte by separate openings lower down. The author concludes that in Chile, where fuel is expensive, and water-power available, this process would be a commercial success.

*Electrodeposition of Copper.*—COWPER-COLES, who has had a long and extended practical experience in the electrodeposition of metals, publishes an article in the December number of the *Electrochemist and Met.*, giving brief illustrated descriptions of a great many processes. He first discusses the plating of iron with copper. The iron surface is freed from scale, oxide and grease by any of the well-known methods, such as sand blasting and pickling, and is then copper plated in an alkaline copper electrolyte which is mostly the double salt of cyanide of potassium and copper. While a considerably higher voltage is required for depositing copper from an alkaline electrolyte than from an acid electrolyte, yet the latter is unsuitable, because iron, when placed in an acid copper electrolyte, is coated with copper by chemical interchange, and the coating is not adherent, and can easily be removed. The electrodeposition of copper upon iron is a large industry. Copper is electrodeposited upon iron hydraulic rams, barrels of guns, tubes, chains, wire, iron sheets for roofing purposes, springs, lamp-posts, ornamental columns, statuary, bridge links, electric light carbons, zinc plates for roofing purposes, wood and other non-metallic substances. Ropper's, Marino's, Crane's and Sneider's methods for coppering ships' bottoms are briefly described. It is mentioned that ships with copper bottoms have been the cause of more than one legal action, due to damage done in shipping when lying in port. A typical case occurred at the port of Leghorn, when an action was brought against owners of copper bottoms lying in the basin of the harbors. The ships and iron vessels lying in the harbor were found to be materially damaged by the galvanic currents set up from the copper bottoms of the wooden yachts, electrical connections being made with the steel vessels through the ropes and hawsers which were used to fasten them to the different buoys. Damage to the steel and iron ships was clearly proven, and the copper bottomed yachts had to be removed from the harbor. A great many different processes are briefly noticed, for instance, copper plating on wood, electrodeposition of copper around glass prisms, copper plating of barrels of guns, steel wire, etc. The difficulty experienced with the steel-cored, copper-coated wire is the rapid corrosion of the steel if the copper is penetrated. The use of copper casings for railway carriages, and the copper plating of printers' rollers is also discussed. The author then gives quite a number of solutions. Roseleur's electrolyte is commonly used, as it may be worked at any temperature. It is prepared by working off 3¼ avoirdupois ounces (92 milligrams) of copper acetate into a thick paste, with a little water; then an equal weight of sodium carbonate crystals is added, with about 1½ pints (0.85 liter of water, and the whole is well stirred for a few minutes. An exchange thus takes place between the sodium carbonate and the copper acetate, with the result that the water contains copper carbonate in suspension, and a sodium acetate in solution. Three and one-quarter ounces of sodium bisulphite are now added in a second 1½ pints of water, and, finally, five pints (2.84 liters) of water, containing 3¼ ounces of potassium cyanide, are introduced. The pale yellow-colored precipitate produced on the addition of the bisulphite will be gradually dissolved on stirring with the cyanide, and should completely disappear after a few minutes, leaving a practically colorless solution. Should it not be so, a little more of the potassium cyanide must be added by degrees, until the decolorization is

perfect. If necessary the bath should be finally filtered. When the bath is used hot, say at 65° C., or 149° F., the quantity of copper may be increased and a stronger current may be used. Pfanhauser has modified this solution. His bath, which gives an excellent coating of copper on iron and zinc, is made up with sodium bisulphite and carbonate, copper potassium cyanide and potassium cyanide, the first two named salts being mixed in advance, with formation of $CO_2$ and $Na_2SO_3$. The following bath was found to give good results: $Na_2SO_3$ (Calc.), 20 grams (308.646 grains); $NaHSO_3$, 6 grams (92.6938 grains); $Na_2SO_4$ (calc.) 20 grams; $Cu(CN)_2KCN$, 30 grams (462.969 grains); KCN, 2 grams (30.8646 grains) per liter (1.7608 pints). The current density should be 0.003 to 0.004 amperes per square cm. (2.8 to 3.7 per square foot), and the pressure between the electrodes, which are 15 cms. (5.9 inches) apart, is 2 to 2.5 volts. Some other solutions are also briefly mentioned. The article is concluded by some notes on the coating of arc lamp carbons, with copper to insure a good metallic contact with the carbon holder, and the coating of zinc with copper. If the solution is used exclusively for plating zinc with copper, the following electrolyte is recommended by Roseleur: Water, 10 quarts (11.36 liters); tartar free, 6.7 ounces (190 milligrams); crystallized carbonate of soda, 15 ounces (425 milligrams); blue vitriol, 6.7 ounces (190 milligrams); caustic lye of 16° Be., ¾ pound (340 milligrams). The solution is prepared by dissolving the tartar and the crystallized carbonate of soda in two-thirds of the water, and the blue vitriol in the remaing one-third, and mixing both solutions; filtering off the precipitate, dissolving in the caustic lye, and adding this solution to the other.

*Electrogalvanizing.*—In the *Elek. Zeit.* of Nov. 12, Grabran describes some experiments made on plating zinc on iron, especially for use with vessels. He experimented with six different solutions, and found that the best results were obtained with a solution containing 1,200 grams $ZnSO_4$, 60 grams $H_2SO_4$, of 24° Baume, and 6,000 grams of water. With a current density of 6 amperes per square decimeter he obtained a solid and firm deposit, the voltage at the terminals being 9 to 10 volts. The "electrochemical equivalent" is given as "0.32 milligram" with circulation; this evidently means that in his experiments he deposited 0.32 milligram per ampere second; in other words, the ampere hour efficiency was nearly 100 per cent. He describes an apparatus for plating the sides of a vessel with zinc. It is especially important that any soldered places of the sides of the ship should be plated with zinc, as otherwise local galvanic action is started. This apparatus might be described as a nozzle through which the electrolyte is circulated. At its end it has a rubber ring with which it is pressed against the side of the ship, while the anode consists of zinc in contact with the electrolyte.

*Nickel Plating.*—In *Erfindungen u. Erfahrungen*, vol. 30, page 518, the following prescription for an electrolyte for nickel plating is given: One kg. nickel sulphate, 715 grams ammonium tartrate, 5 grams of tannic acid, dissolved in ether, are mixed in 3 to 5 liters of very hot water, filtered and diluted with 17 to 15 liters of water. The solution must be neutral and is stated to be suitable for plating nickel on any metal.

*Organic Matter in Plating Solutions.*—In the December issue of *Metal Industry*, Sperry discusses the effect which the presence of organic matter in plating solutions has upon the deposit. Early in the history of copper refining it was found that certain kinds of varnishes used to protect the wooden vats greatly influenced the character of the deposit. It was found that benzoic acid, added in extremely small amounts, to a sulphate of copper solution would give a bright and tough deposit which otherwise would be dark-colored and granular. To get with a high current density a good copper deposit, gelatine may be added to the solution, in the proportion of one part of gelatine in 30,000,000 parts of solution. If too much gelatine is added the result is worse than if none at all is introduced. A solution of gelatine in dilute nitric acid is employed for the purpose. It is stated that it has been found by a certain copper producer that an infusion of oak-wood—which he calls "wood-tea"—accomplishes the same result. It likewise is said to prevent the antimony from coming down with the copper and contaminating it.

*Electrolytic Drilling and Slotting Process.*—At the present time armor plates are often drilled by means of an electric arc, the plate being connected to one pole of the electric generator and the carbon to the other; the carbon is held over the spot to be drilled, and the iron melted out. Another process consists in softening the plates locally by applying heat by means of an electric current, the portion to be drilled being made the resistance in an electric circuit; it is then drilled in the ordinary way. The oxy-hydrogen flame is used in a similar manner, both for the actual drilling and softening. An elaboration of the oxy-hydrogen process consists of blowing oxygen at a high pressure against the portion of steel being heated by the oxy-hydrogen flame, so that the heat of combination will yield the amount of heat necessary to melt the adjoining parts, the high pressure of the oxygen carrying all the molten iron with greater velocity than the heat can be conveyed from them. It is claimed that by this method a cold steel ingot, about 15½ inches in thickness, can be perforated in about 3 minutes. In the October issue of the *Electrochemist and Met.*, Cowper-Coles describes an electrolytic drilling and slotting process which he has worked out. In his first experiments the electrolyte was projected on to the iron to be drilled, a current of electricity being sent from the metal to be drilled through the jet of liquid and back to the generator. While this method gave fairly satisfactory results, yet the holes were not sufficiently true. A nozzle was then constructed, through which the electrolyte is being rapidly circulated around a baffle plate, placed in the center of the nozzle. A pointed rod, fitted in a gland, is so arranged as to be near the end of the baffle plate. The rod forms the negative electrode, on which the iron is deposited as a powder, to the high current density, and is washed away by the rapidly circulating electrolyte. The end of the nozzle is fitted with a removable washer, the shape and size of which determines the shape and size of the pole to be drilled. While some of the best results in drilling iron have been obtained with a solution of sulphuric acid, good results have been obtained by ordinary salt water.

*Electrolysis of Water.*—In an illustrated article, published in *La Machine* (Geneva) vol. 5, pages 7 and 33, Fiersot describes the apparatus of Siemens & Halske for the electrolysis of water in which a 10 per cent solution of potassium carbonate is used as electrolyte. One hundred and thirty-four grams of water are decomposed per kilowatt-hour. By heating the electrolyte the output may be increased by 8 per cent. The electrolytic oxygen thus produced is in the average 97 per cent pure, while the hydrogen contains one per cent of oxygen.

*Electric Furnace.*—The November and December issues of *Elektrochem. Zeit.* contain the conclusion of the illustrated serial by Minet on the development and the applications of the electric furnace. He describes the aluminium furnaces of Kiliani, Hall, Gooch and Borchers; the magnesium furnaces of Fischer, Graetzel, and Borchers; and the sodium furnaces of Graubau, Borchers and Becker.

*Fixation of Atmospheric Nitrogen.*—A concise summary of recent investigations in this line is given in *Zeit. f. Elektrochemie*, October 29.

### Theoretical and Experimental.

*Electric Potentials of Some Strong Oxidizing Agents.*—In a paper published in *Zeit. f. Elektrochem.*, November 5, Scorai first gives a review of the work of various experimenters who tried to determine the potential of strong oxidizing agents dependent on the concentration of the hydrogen ions in dilute solutions. All of them experienced great difficulties, since it takes a longer time before a constant reading is obtained and the readings do not agree well together. He has now investigated whether better results can be obtained in

concentrated solutions, and has investigated under which conditions one may rely upon getting constant e. m. f's., and always the same value. The problem is intimately connected with the question of the reversibility of the reaction. He experimented with various strong oxidizing agents, like peroxide of manganese, permanganate of potassium, and persulphate of sodium in 1 normal, 12 normal, 22 normal, and concentrated $H_2SO_4$. While, in the cases investigated by him, no practical reversible reactions take place, yet constant values of the potential can be obtained. The value of the potential is constant for a long time, and does not, therefore, depend upon the time. If an electrode is replaced by a new one, the old values of the potential are soon obtained again. In general, the e. m. f. is independent of the material of the inert electrode. While with chromic acid the potential value was found to decrease slightly, as a result of stirring, yet the old values were soon reached again. He concludes that the potential values measured by him are really constant and not accidental, that they can be reproduced, and that they probably represent values characteristic of the oxidizing agents used.

*Electric Resistance Furnace for the Laboratory.*—In the *Journal de Chimie Phys.*, September, GUNTZ describes the following construction of an electric resistance furnace for laboratory use. On a tube of porous earthenware, which serves as the heating tube, he applies a layer of 5 mm. thickness of aluminate of magnesium, which does not attack platinum at a high temperature. It contains about 8 parts of weight of MgO to one of $Al_2O_3$. On this layer of magnesium aluminate he winds a platinum wire of about 0.3 mm. diameter, the distance between its turns being about 5 mm. Around this he applies another layer of aluminate of magnesium. The whole is covered by a layer of asbestos. The two terminals of the platinum wire, which are fixed by means of a screw on the outside layer, serve as connection for the current. The apparatus is said to stand a temperature of 1,300° to 1,400° C., with a consumption of 700 volts, the tube being 25 cm. long, and having a diameter of 5 cm.; its cost is low.

*Electrochemical Laboratories.*—Two descriptions are found in the *Electrochemist and Met.* of October, the one by PERKIN, of the electrochemical installation at the Borough Polytechnic Institute in London, the other of the general arrangement of the Metallurgical Institute of Aix la Chapelle in Germany. Perkin derives his working current from twelve storage cells, with 80 ampere-hours capacity, which may be connected either in series or in parallel or part in series and part in parallel. For regulating purposes he uses resistances made from insulated platinoid wire, wound on asbestos-covered brass tubes. The advantage of winding on tubes is that a current of air passes through them and serves to keep the resistance cool. The contact is a double-sliding one, and a connection is made with the resistance wire by removing the insulation from the upper and lower surfaces of the wire. Each of these resistances is about 20 ohms, and will carry a current of about 3 amperes without unduly heating. For carrying heavier currents he uses resistances made of insulated segments of copper strip, clamped closely together and connected up in series by means of spirals of platinoid wire. The resistance is regulated by means of a sliding key contact. This resistance carries from 4 to 5 amperes without becoming unduly hot. Liquid resistances are very convenient, but the solution easily becomes very hot and evaporates away.

*Separation of Iron from Manganese.*—In the *Chem. Berichte*, vol. 36, page 2,716, KOESTER discusses the electrolytic separation of iron and manganese. Difficulties are experienced here since always some quantities of iron are carried away with the manganese, which is deposited as peroxide. For smaller quantities of manganese, Classen recommends to reduce the formed peroxide of manganese by an addition of oxalic acid, so that the manganese is not deposited before all the iron has been separated. If, however, manganese is present in larger quantities, the oxalic acid is not sufficient to retard the deposition of manganese. The present author has found phosphoric acid to be an excellent reducing agent in this case.

*Lighting of Ions.*—The paper of BOLTON read before the International Congress for Applied Chemistry (ELECTROCHEMICAL INDUSTRY, 1903, page 566) is printed in full under the title "on lighting of the electrodes, and a new spectroscopic method" in the *Zeit. f. Elektrochemie*, November 19. A great number of spectroscopic results are given in form of diagrams. The number of December 17, of the same journal, contains two communications by Hoppe and Voller, claiming priority of the invention of the method.

*Electrochemistry.*—In two further installments of his series on the development and present condition of electrochemistry (*Electrochem. Zeit.*, November and December), NEUBURGER gives a review of the electrochemical theories before Faraday, and discusses especially the theory of Berzelius.

*New Journal for Physical Chemistry.*—The first number of a new journal has just appeared. The title is *Physikalisch-Chemisches Centralblatt* (Physico-Chemical Review). The editor is M. Rudolphi, and the publishers are Gebrueder Borntraeger, in Berlin. The journal will not publish original articles or papers, but is intended to be a comprehensive review of progress in physical chemistry, giving quick, thorough and concise abstracts of the original articles published in various countries in this field. In order to be complete it must be international, and for this reason a novel departure is made, in so far as the abstracts are given either in German, or English, or French. As far as possible the abstracts will be furnished by the authors themselves. As regular contributors, are mentioned on the title page, the following Americans: Bancroft, Goodwin, Jones, Kahlenberg, Loomis, Noyes, T. W. Richards and L. R. Morgan. The first number was published on December 15, and comprises thirty-two pages, on which abstracts are given of seventy-nine papers. The journal is to be published twice a month.

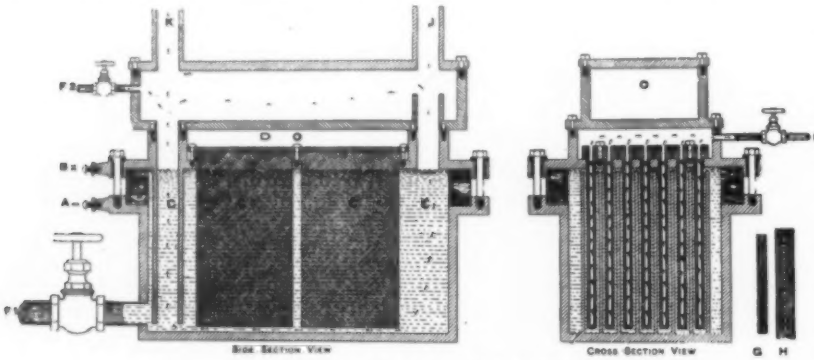
### BATTERIES.

*Electrolytic Formation of Lead Peroxide from Lead.*—The *Centralblatt f. Accumulatorenkunde* of September 15, October 1 and 15, and November 1 and 15, contains a long article by ROKOTNITZ, on the electrolytic production of lead peroxide from lead. His results may be summed up as follows. In sulphuric acid solution the output of peroxide is very small, and nearly independent on the concentration; the ampere-hour efficiency is less than 0.3 per cent. If the electrolysis is first conducted at 2 volts for producing lead oxides, and then continued at a higher voltage, the efficiency is only very slightly better, being still below 0.5 per cent. The efficiency is improved, if the metallic lead is first treated in an ammoniacal solution; a treatment in ammoniacal solution for eighteen hours, and in sulphuric acid for thirty hours gave an efficiency slightly above 2 per cent, while a treatment of twenty-four hours in ammoniacal solution, and twenty-four hours in sulphuric acid gave an efficiency of 3½ per cent. The efficiency became much better, if such substances were added which first produced another lead compound, from which peroxide could then be formed more easily. Additions of potassium chlorate and potassium sulphate in such a degree that the quantity of the "precipitation salt" corresponds to the electrochemical equivalent, and that of the "solution salt" to the maximum conductivity of the electrolyte, produced an efficiency of 80 per cent. (This is the method of Luckow: the author used 46.7 grams of potassium sulphate and 30 grams of potassium chlorate for one liter of water.) If a smaller amount of chlorate was used with circulation of the electrolyte, the efficiency was smaller, but still good (63 per cent); with the same electrolyte, without circulation at a temperature of 60° C., it was 52 per cent; at ordinary temperature of the room 48 per cent; at 0° C. 28 per cent. If, in the same electrolyte perchlorate is substituted for chlorate, and the electrolysis is made at the temperature of the room, the efficiency is 39 per cent. Some better results were again obtained by

addition of nitric acid (49 per cent). A 7½ per cent solution of 95.5 parts of ammonium sulphate and 0.5 part chlorate in dilute sulphuric acid gave an efficiency of 32 per cent; if perchlorate was substituted in this case for chlorate, the efficiency was reduced to below 4 per cent. Alkaline solutions gave worse results than acid solutions; the best electrolyte of the former being sodium hydroxide, which gave an efficiency of 19 per cent. In the numbers of December 1 and 15, of the same journal, continuations are published of the serial of Peters, the publication of which was begun long ago, but was discontinued for some time, in which he gives the results of laboratory tests on the electrolytic formation of lead peroxide from lead. The end of the serial seems not yet near, nor is any summary given of the results.

*Light Storage Batteries.*—While by far most of the storage batteries placed on the market by the manufacturers are used for stationary purposes in lighting or traction stations, yet the increasing interest in automobilism has placed before the battery designer a new problem, that is to develop a light accumulator. The development of the light accumulator since 1900 is reviewed by Joly in an illustrated article in the October issue of *Electrochemist and Met.* Some notes are given concerning the following batteries: Phenix, Max, De Dion Bouton, Tommasi, Contal, Exide (Electric Storage Battery Co.), Edison, Hart, Oppermann, Leitner, Elieson, Lithanode, Rosenthal, Poppenburg, Progress, Garassino, and a few others. Concerning the Contal battery (Accumulator Electricia) it is said that its cost is moderate, and that it has a remarkably long life under the severe conditions of road traction. The plates are 103 x 120 mm. and 3.5 mm. thick, and are made in two pieces, riveted together in the mechanical pasting. Triangular bars divide each side into 252 small squares, and the plates are perforated with 252 holes, in the center of each square, respectively. In tests which were made in the Laboratoire Central in Paris in 1901, and which are said to have since been confirmed by daily practice, a 21-plate cell, weighing 13 kg., gave 150 ampere hours and 290 watt hours, at a rate of 49.2 amperes; 194 ampere hours and 384 watt hours at a rate of 32.7 amperes; 218 ampere hours and 434 watt hours at a rate of 18 amperes; 210 ampere hours and 425 watt hours at a rate of 14 amperes. Each cell carries two taper terminals, which the connections from cell to cell are made to fit, thus assuring a good contact right through.

*Electricity Direct from Carbon.*—The old problem of devising a carbon cell continues to attract inventors. One of the latest aspirants to honors in this line is J. H. Reid, whose patents were abstracted in Electrochemical Industry, December, 1903, pages 591 and 592. He has now given a public demonstration of his cell at Newark, N. J., an account of the exhibition being given in *Electrical World and Engineer,* December 12. Briefly, the method consists in conducting a fuel gas into a porous receptacle pervious to gas, but impervious to liquid; maintaining a heated electrolyte at the opposite face of the receptacle; supplying oxygen to the heated electrolyte, and providing conductors for the developed electricity from the porous receptacle and from the liquid electrolyte. The cell is a cylindrical iron vessel filled with an electrolyte composed of sodium hydrate, calcium chloride and iron oxide, the electrolyte being maintained at a temperature of 390° F. Penetrating into the electrolyte, and insulated from the iron are hollow electrodes, made of carbon. The carbons are of positive polarity, and the iron pot of negative polarity. Fuel gas is forced into the hollow carbons, and the contention is that it percolates through the porous walls of the carbons, the carbon and hydrogen of the gas uniting with the oxygen in the electrolyte or in the carbon wall, resulting in the production of electricity. At the demonstration, illuminating gas, mixed with air, in the proportion of one part of gas to 40 of air, was used, and the electrolyte was heated with illuminating gas. An e. m. f. of 0.9 volt was developed and maintained fairly constant, so long as the gas was passed through under the proper pressure, and the electrolyte was maintained at a temperature of 390° F. The gases escaping at the top of the cell were said to contain water vapor, carbon dioxide and carbon monoxide, and the inventor intends to return them to the combustion chamber, so as to recover the heat value of the carbon monoxide. The cell recovers very rapidly from the effects of short-circuit. The form which a commercial plant will take is illustrated diagrammatically by Figs. 1, 2, 3. Fig. 1 represents the containing vessel, which is the negative pole; *B*, the aerating and exhaust part of the apparatus being the positive pole; *C* are the porous electrodes directly-connected to the positive pole, while *D* is the gas chamber into which gases are forced and allowed to percolate through the porous electrode into chamber *E*, which is filled to line *B*, with an electrolyte. This electrolyte is an oxidant. The cock marked *F*1 is for convenience in drawing off the electrolyte, and *F*2 is a water cock for cleaning out the aerating and expansion chamber. In Fig. 2 *F*3 is a cock controlling the flow of gas, *G* is the bottom view of the electrodes, *C C h* is the top view showing gas inlets to electrodes *C C*; *I* shows the iron electrodes connected to *A* and forming the negative electrode in the electrolyte. The arrow marks in this cut show the flow of gas, and in Fig. 3 of the electrolyte to and from their openings; *J* represents the




FIGS. 1 AND 2.—REID GAS BATTERY.

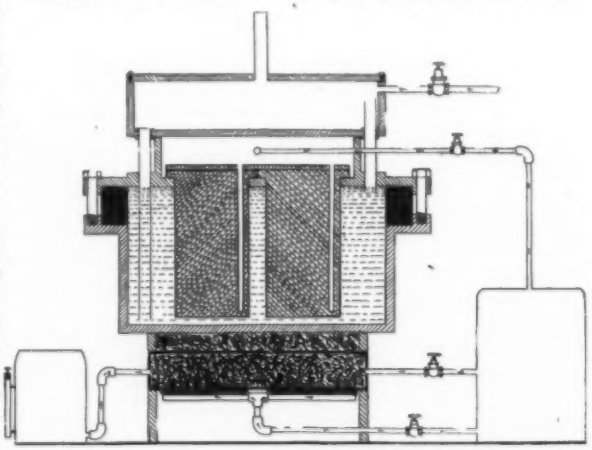


FIG. 3.—REID GAS BATTERY.

exhaust, and *K* is an intake of free air to maintain the balance of oxygen in the electrolyte. It is stated that a 100-hp outfit made up of ten cells will be exhibited publicly some time in January. This, it is claimed, will be a practical and commercial apparatus, and will be submitted to a committee of experts. It is stated that it will occupy a space 8 x 8 x 10 feet long, and will include, besides the cells, a complete gas generating plant. As the e. m. f. will be but 10 volts, a current of 7,460 amperes will be generated. (A critical discussion of the scheme of the Reid cell will be found in an article of Mr. C. J. Reed, published on another page of this issue.)

### MISCELLANEOUS.

*Estimating Gold in Working Cyanide Solutions.*—The determination of gold in cyanide solutions by evaporation and fire assay, although possessing considerable accuracy, is an extremely cumbrous and lengthy process, especially when very weak solutions are dealt with. In consequence of this fact control of the zinc precipitation of gold is rendered difficult, for the reason that the assay of the liquor from the foot of the zinc boxes is frequently not obtainable before the next day, by which time the solutions may have become seriously deranged, for example, gold-bearing solution may have been used for leaching. In the *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, of September, MOIR describes a method of detecting traces of gold in the state of auro-cyanide in less than twenty minutes. The principle is "to precipitate the gold by means of the strongest available galvanic couple in a medium which destroys the cyanides and keeps the ferro-cyanides and other common impurities in solution. The metallic gold is then dissolved in aqua regia and tested for with stannous chloride in the usual way. The different intensities of color obtained are sufficiently distinct from one another to enable an estimation of the gold, within a few grains, to be made by comparison with a graduated color-wedge, or a set of standard colors, and after a little experience one can dispense with these and estimate within less than 0.2 dwt. by eye alone." The process, in detail, is as follows: 100 cc. of the cyanide solution is poured into an evaporating basin (of not more than 300 cc. capacity), treated with one or two grams of sodium peroxide, and boiled for two minutes to destroy the cyanide. The quantity of peroxide and length of time of boiling is varied according to the amount of free cyanide present. Next, two drops of lead acetate solution (10 per cent) are added, whereon a brown spot of $PbO_2$ forms and re-dissolves, showing whether enough $Na_2O_2$ has been employed. Next, the flame is removed and a small quantity (about 0.1 gram )of aluminium powder is added and the mixture vigorously stirred until hydrogen ceases to come off. If the aluminium is pure the liquid will not require to be heated. What happens is that metallic lead is first precipitated and the aluminium-lead couple electrolyses the auro-cyanide, so that finally we have a black precipitate, consisting of lead and gold, whilst the liquor no longer contains cyanide. The mixture is filtered through a small paper, and the dish rinsed out into it. This is very easy, with so alkaline a solution. The filtrate is rejected. Next, 10 cc. of aqua regia is warmed until it turns yellow and poured into the paper, and the filtrate is collected in a test tube, boiled and poured through the paper again. This is repeated until the filter paper is perfectly clean, whereon it is washed out with a small quantity of water. The yellow filtrate is then treated with strong stannous chloride solution, added drop by drop, until the yellow color has faded. If the original cyanide solution contained over 5 dwt. of gold, the purplish blue shade appears at once, but if only a few grains of gold per ton were present the mixture must stand a few seconds. After half a minute the full intensity is attained, and the comparison with the standards is made. For exact work the solution is poured into a cylinder exactly one inch in internal diameter, and made up to a definite volume, say, 15 cc., with water, before making this comparison. The purple solution fades through oxidation on keeping, and, therefore, cannot be used for a standard. He, therefore, uses a permanent imitation of the shade, made by adding copper sulphate solution to cobalt nitrate solution until the exact tint is obtained; the mixture is diluted for use and standardized by the results of the foregoing process applied to cyanide solutions of known gold-content.

For the range between 0.5 and 2 dwt. per ton, the most convenient standard is an "indigo-prism" or triangular bottle, which, when filled with the above-colored fluid, affords a gradually varying thickness of liquid, and can be graduated empirically once for all, so as to read directly in dwt. per ton. This is held horizontally and moved across the cylinder at the level of the gold-containing liquid until its color is matched, when the value is read off. Some practice in matching colors is required in order to read to 0.1 dwt., but without practice one can read to 0.2 dwt. Of course, it is more satisfactory to keep a set of standard tubes (15 cc. in tubes of constant diameter differing in value by, say, 3 grains), but this takes a longer time to prepare. For quantities under 10 grains per ton it is best to look down the tubes and make the comparison exactly as in "Nesslerising." The lower limit is about two grains per ton, but if one starts with a larger quantity of the original cyanide solution than 100 cc. is proportionately increased, as the gold is still concentrated into the final 15 cc. Thus, if 500 cc. be taken, the limit is about 0.4 grain per ton (one part in thirty-five millions.) It should be noted that the differences of intensity are less marked for the darker solutions; anything over 3 dwt. per ton gives a nearly opaque solution. Therefore, if the solution to be tested is known to be strong, only 50, or even 25 cc. should be taken for the experiment, diluting to 100 cc., and multiplying the result by two or four, respectively. As a check against the occurence of incomplete precipitation of the gold, it is advisable to test the filtrate from the lead with $FeSO_4$ and HCL for cyanide, which should be absent in a successful experiment. The best mixture for aqua regia is 100 cc. concentrated nitric acid, 300 cc. concentrated hydrochloric acid, and 400 cc. water. For the benefit of those who have not sodium peroxide at their disposal, the author has introduced the following modification. A solution is made of 30 per cent NaOH and 0.1 per cent litharge. Ten cc. of this is boiled with 100 cc. of cyanide solutions for five minutes, then the aluminium is added and the rest of the process is the same.

*Welding Aluminium.*—The problem of making an efficient and durable aluminium joint is of great importance for the practice. In the November number of the *Electrochemist and Met.*, COWPER-COLES gives some illustrated notes on the welding of aluminium. He claims that soldered aluminium joints have proven unsatisfactory, and describes the welding processes of Dick, Heræus, Emmé, Schmidt, and Jones' process for welding aluminium tubes. He thus describes at greater length his own process, in which no flux or solder is used, and which does not necessitate the hammering of the joint when in the semi-fluid state. The process is stated to be especially suitable for wire rods and tubes, and other turned or rolled sections, and consists in placing the parts to be soldered, after being faced off square in a machine fitted with clamping screws which are capable of moving horizontally on suitable guides. The motion of the clamping screws is controlled by levers. The aluminium to be welded is heated by means of an ordinary benzine lamp, and as soon as the rods have arrived at the necessary temperature, slight pressure is supplied to the levers mentioned before, which causes them to unite, and a ring of metal is squeezed out. This ring is largely composed of aluminium oxide, and acts as an insulating supporting collar, the molten metal being retained within this collar. The weld is then instantaneously quenched by turning a handle attached to a screen which allows water under pressure to be projected on to the joint from a reservoir. The same handle which turns the water on, places a screen in front of the heating flame, the rod is then removed from the machine and

the collar is filed off. The joint is claimed as strong as the rest of the metal.

*Electric Pyrometer.*—While in the early days of the electric furnace the intention always was to get as high a temperature as possible, the later development of furnace design has led to an elaboration of methods for controlling the temperature in the furnace, so that it remains between given limits. The reason is that the temperature is generally the main factor which determines the end product of a furnace reaction. Under these circumstances the importance of reliable means for measuring the high temperatures in a furnace correctly is quite evident. The London *Electrician*, of November 6, contains an illustrated description of a pyrometer made by a British firm. It consists of a coil of platinum wire, wound upon a cylinder of refractory material, and usually fixed at the end of a long closed iron tube, where it is protected by a platinum shield, for measuring the resistances of the coil, in order to ascertain the temperature. The temperature is thus measured by determining the change of the electric resistance with the temperature. Two different arrangements are used. One comprises a differential galvanometer and a set of resistance coils, and gives readings in ohms and the temperatures corresponding thereto are ascertained by means of special tables. The second arrangement, which is shown in Fig. 3, is a combination of a simple d'Arsonval galvanometer and a Wheatstone bridge, with a circular resistance and sliding contact, and it gives readings directly in thermometric degrees. It is claimed that both types give very accurate readings. Their principal field of application lies with iron, steel and similar processes, the temperature of which has to be constantly watched and regulated. In the instrument of the first type described above, a change of the resistance from 10 ohms to 44.9 ohms, corresponds to a rise in temperature from 58° F. to 2,204° F.

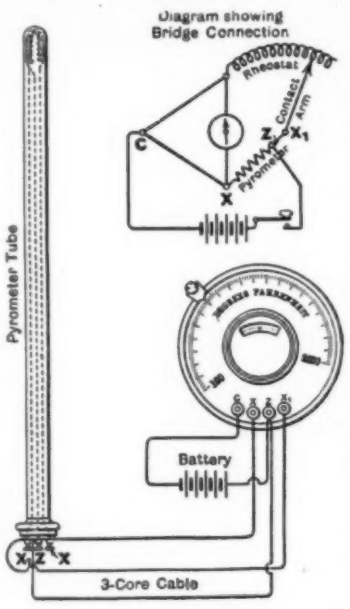



FIG. 3.—PYROMETER.

*Acetylene.*—A paper by Kuchel, giving practical notes on the construction of acetylene central stations, and of the network of tubes for distribution of the acetylene is given in the *Zeit. f. Calciumcarbid Fab.*, November 20 and 27. The numbers of December 4 and 11, of the same journal, contain a description by Fouche of a new acetylene-oxygen burner for soldering purposes.

*Gibbs.*—The December number of the *Physical Review* contains, from the pen of J. E. Trevor, an account of the life of Josiah Willard Gibb, with a concise analysis of the contents of his most important thermodynamical papers.

# ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

By George P. Scholl, Ph. D.

Electric Furnace and Furnace Products.

*Metallurgical Process.*—O. W. Brown, Bloomington, and W. F. Oesterle, Marion, Ind. Patent 742,830, November 3, 1903. Application filed May 14, 1903.

The process relates specially to the treatment of zinc blende in the electric furnace. In carrying out the process the inventors state that they mix carbon (coke or coal) and lime with the zinc blende, in proportions varying with the purity of the ore and the by-product desired. The mixture is placed in the electric furnace and heated in the usual manner to a sufficiently high temperature, whereupon, as the inventors say, the zinc is reduced to a metallic form and volatilized out and condensed in the usual way, while the carbon and the calcium are saved, together with the sulphur, in the form of calcium carbide and carbon disulphide.

*Method of Melting Glass.*—J. T. C. Kessmeier, Washington, Pa. Patent 745,863, December 1, 1903. Application filed November 14, 1902.

The object of the invention is to provide means whereby glass may be rendered so soft and fluid that it can be made to flow from a tank or furnace into molds with deep and narrow cavities. The glass is melted in a tank, furnace, pot or other suitable receptacle by the heat derived from burning fuel; it is allowed to flow from the melting furnace, and as it flows it is superheated to a very high degree, 3500° F., or more by means of an electric current, so that it will reach the molds in a state of extreme fluidity. The tank is of ordinary construction, and is provided with a cylindrical conduit through which the glass flows when a plug, which closes the conduit ordinarily, is withdrawn. On opposite sides of this conduit there are arranged holes through which pass carbons, which are fed against each other by a mechanism, the same in construction and operation as the feeding mechanism of an electric arc lamp. A current of approximately 5 amperes for each square millimeter of electrode surface at 300 volts is conveyed to the carbons. When a casting is to be made, the plug is withdrawn from the conduit and the carbons brought together so as to form the arc. The glass, as it flows through the conduit, comes in contact with the carbons and is superheated and rendered very soft, so that it will flow into the molds like molten metal. The mechanism for feeding the carbons towards each other, as they are consumed, is only necessary when very large castings are to be made, or when the molds are filled in rapid succession, as the arc will be maintained for considerable time, before the carbons are consumed to such an extent as to break it.

*Electric Furnace.*—W. S. Franklin, South Bethlehem, Pa. Patent 742,852, November 3, 1903. Application filed December 3, 1900.

The furnace described in the specification is shown in the accompanying Fig. 1. It consists, essentially, of a block of masonry A, in the lower portion of which is formed a pear-shaped chamber B, which, at its upper end, connects with a cylindrical passage C. The upper end of the latter is widened out in the form of a cone, which serves for the introduction of the materials to be treated in the furnace. A layer of carbon, metal or other suitable conducting material, preferably in the form of plates, is built into the wall of the furnace and extends around the circumference of the chamber B. This layer forms one of the electrodes of the furnace. The second electrode F is constituted by a bar of carbon, metal or other suitable material, and it has a number of teeth $f^3$ on its circum-

ference, which point downwards. H and G are tapping holes. In the operation of the furnace, a portion of the chamber B is stated to be filled with a molten electrical conductor I, which has a high electrical resistance. Slag or glass are said to be suitable for such purpose. The upper electrode can either be dipped into this conductor, in which case the heating is mainly done by resistance, or it may be raised above its surface, and in this case the heating will also be accomplished by the arc formed between the electrode and the surface of the molten material. The electrode is shown supported upon an eccentric, so that it can move up and down, and its downward stroke carry the charge down. In the reduction of iron ores the material for the molten conductor is preferably slag. The usual charge containing the ore is fed into D, preferably at intervals, as the latter method is stated to enable the charge of ore, coal, limestone, etc., to be fed separately, and to be accurately regulated in quantity. The operation is described as follows: "As the charge passes downward the ore is reduced during its descent by the heat ascending from the molten conductor, or from such conductor and the arc, according as the carbon rod is immersed or not in the molten conductor.

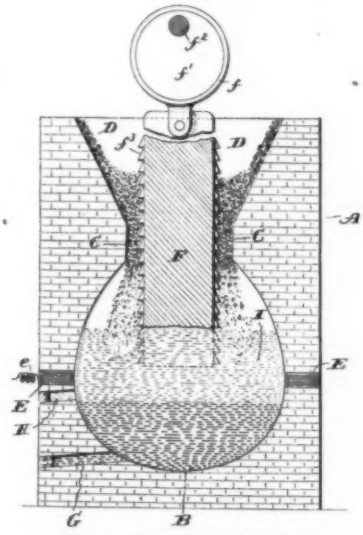


FIG. 1.—ELECTRIC FURNACE.

When the ore reaches the intensely hot slag, it melts and filters through the slag to the bottom of the receptacle B, where it collects. The iron is drawn off as desired through the lower vent, and the slag is kept at the proper level through the upper vent." If the furnace is to be used for glass-making, the lower portion of the chamber B is lined with carbon, or other conducting material.

*Process of Producing Carbon Chlorides and Silicon.*—F. J. Machalske, Brooklyn, N. Y. Patent 745,637, December 1, 1903. Application filed September 16, 1903.

The process consists in reacting on a carbon compound, such as carbon bisulphide or methane, with a chloride of silicon, usually the tetrachloride, under such conditions that the silicon and carbon interchange and the resulting carbon chloride is driven off. The reaction is effected in the electric furnace in a non-oxidizing and dry atmosphere. In the case of carbon bisulphide the reaction produces silicon bisulphide, which may be readily reduced to metallic silicon by heating it with carbon. The apparatus, used for carrying out the process comprises, in the first place, an electric furnace, composed of a stack lined with magnesia brick, suitably provided with electrodes, preferably of metallic silicon. Charge opening, outlet and tapping-hole are provided also. For the production of silicon tetrachloride the furnace is charged with a water-free mixture of silica, preferably sand, and an alkali chloride, preferably sodium chloride. An electric current is then passed in order to heat the mixture to a sufficient temperature to effect the reaction. The gaseous silicon tetrachloride escapes and the molten residue of sodium oxide is tapped off. The silicon tetrachloride is conducted into a mixing chamber, which is situated above a second electric furnace, of similar construction to the first. This furnace is used to produce carbon bisulphide, from a charge of carbon and sulphur. The vapors of the carbon bisulphide rise and mingle with those of silicon tetrachlorides, and the resulting mixture passes into another electric furnace. The latter has the purpose of heating the mixed gases to the temperature necessary to effect the reaction between them. One or more pairs of electrodes, which may be of carbon, platinum, etc., are arranged to heat the gas mixture by means of arc sprung between the ends of the adjacent electrodes. The carbon chloride finally escapes through an outlet flue, and the silicon sulphide produced may be withdrawn through the tapping hole. The latter may be conveniently employed by charging it, mixed with an equivalent amount of carbon, into the second electric furnace, instead of or as an addition to the charge of carbon and sulphur. The metallic silicon produced by the reduction may be drawn off through the tapping hole of this furnace. It is stated that methane or other carbon compounds may be substituted for carbon bisulphide as a source of carbon. When a mixture of one combining weight of silicon tetrachloride and methane is heated to the proper temperature in the third furnace, the silicon and carbon interchange according to the equation, $SiCl_4 + CH_4 = CCl_4 + SiH_4$. This hydride of silicon may be advantageously used for the production of finely divided silicon carbide or carborundum, by burning the hydride in an atmosphere of carbon dioxide. The reaction taking place then may be expressed by the equation, $SiH_4 + CO_2 = SiC + 2H_2O$.

APPARATUS AND PROCESSES FOR THE ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

*Electrolytic Apparatus.*—E. Hannon, Brussels, Belgium, assignor to the Solvay Process Co., Syracuse. Patent 742,863, November 3, 1903.

*Electrolytic Process.*—E. Hannon, Brussels, assignor to the same. Patent 742,864. Both applications filed October 4, 1898.

The process and the apparatus described in the two specifications are primarily intended for the electrolysis of alkaline chlorides by means of mercury. The apparatus is illustrated in Fig. 2. It consists of a receptacle A, which contains the

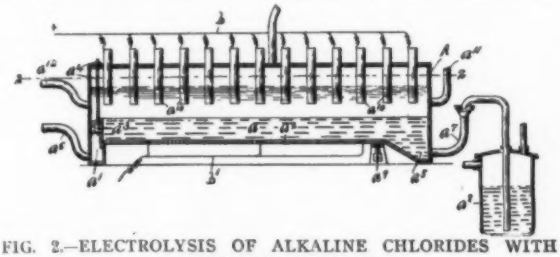


FIG. 2.—ELECTROLYSIS OF ALKALINE CHLORIDES WITH MERCURY CATHODE.

electrolyte, and a fluid electrode, such as mercury. The latter is admitted into the reservoir $a^5$, situated within the above receptacle, through a pipe $a^7$ entering at the bottom. This pipe is in connection with a supply chamber, from which a suitable quantity of mercury can be forced by pressure. At the other end of the apparatus is a wall $a^6$, the height of which can be regulated by screws $a^4$, which wall divides the vessel into two compartments, a, a'. The level of the mercury in a' is lower than that in a. The upper portion of the mecury, which contains most of the amalgam, overflows into the compartment a', whence it is removed by means of pipe $a^8$. The arrangement of the anodes $a^{10}$, and the supply and discharge pipes for the electrolyte, are clearly shown in the illustration. The screw $a^9$,

fixed on the bottom of the apparatus, is provided for the purpose of tilting the latter if it is desired to remove all the mercury. Means for discharging the amalgam are not shown.

*Manufacture of Sodium.*—T. Ewan, Glasgow, Scotland. Patent 745,958, December 1, 1903. Application filed April 18, 1903.

The process is briefly described by the inventor as follows: "Sodium hydroxide is fused in a suitable vessel, and a current of electricity passed through it between electrodes, between which a porous diaphragm is placed in such a way, that the electrolyte surrounding the cathode is prevented from mixing readily with that surrounding the anode. The porous diaphragm is made of alumina, or of sodium aluminate, or of mixtures of these substances. Sodium, together with a very small quantity of hydrogen, is formed at the cathode. Oxygen and water are formed at the anode. The removal of the water from the fused electrolyte surrounding the anode is facilitated by passing a current of air or other suitable gas through or over it."

*Electrode and Conductor.*—C. E. Acker, Niagara Falls. Patent 743,410, November 10, 1903. Application filed June 5, 1902.

The invention relates to the construction of a carbon electrode designed specially for use in electrolytic operation, where high-current densities are employed. It is illustrated in Fig. 3, and consists essentially of a carbon block 1, the lower surface of which is provided with grooves. The latter serve the purpose of facilitating the escape of gases. 2, 2 are carbon shanks, protected by tubes 4, 4 of fire clay or other refractory material, in order to prevent access of air to the heated carbon. The carbon shanks are connected to a conductor 3 by means of the rods 5, 5 and the yoke 6. In order to protect also the juncture between the carbon shanks and the metallic conductors, slabs of scrapstone are united by plates or grids 8 into a casing, the interior of which is filled with cement 9. This refractory casing is of somewhat greater area than the block 1, so that, when a series of electrodes is assembled in a furnace, the carbon blocks are sufficiently far apart to permit the furnace charge to be fed between them. A specific example of the use of the electrode is given, when the electrolyte is sodium chloride, which is maintained in fusion by the current. The carbon blocks may be 8¾ inches wide by 13½ inches long by 4 inches thick, the lower or working face of each having an area of approximately 118 square inches. The current density may vary from 20 to 25 amperes per square inch of working face. For an electrode block of this size and the above current density, the shank should consist either of one carbon rod, 6 inches in diameter, or of two rods, 4¼ inches each in diameter. It has been found that the best material for the purpose is a carbon composition, which is not moulded, but forced through dies under heavy pressure. Both the anode blocks 1 and the shanks 2 are formed of this material, which may be graphitized to increase their conductivity and to facilitate tooling.

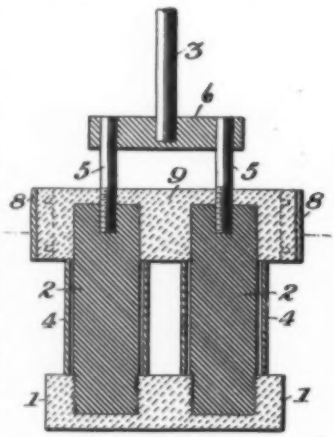


FIG. 3.—ELECTRODE.

*Coating Glass or Fabrics.*—H. Keppler, Brooklyn, N. Y. Patent 743,522, November 10, 1903. Application filed February 21, 1903.

In carrying out this method for depositing metal on glass, fabrics and other material, the inventor first mixes medium bronze lacquer with "illuminous powder and applies it evenly over the surface of the glass. This process gives the surface a frosted appearance and makes it act as reflector, f. i., when applied to the upper half of an electric light globe. In coating fabrics the lacquer only is applied and the powder omitted. The second step consists in mercerizing white rubbing varnish and applying the latter evenly over the first mixture. This surface before drying is dusted over with gold bronze powder and dried. The final step consists in subjecting the article thus coated to a copper bath, after which it may then be painted or enamelled. When the process is applied to laces or fabrics, the inventor states that the latter materials retain to a surprising degree their pliability.

*Extracting Chromium from Chrome Iron Ore.*—R. Suchy and H. Specketer, Griesheim-on-the-Main, Germany, assignors to Chemische Fabrik Griesheim Electron. Patent 743,668, November 10, 1903. Application filed February 6, 1903.

The inventors have found that chromium can be extracted from the chrome iron ore in a very simple manner, by treating the latter in hot acid solutions with oxidizing agents, such as peroxide of manganese, permanganate, chromic acid, etc. They explain the dissolving action of these agents by their oxidation of the protoxide of iron contained in the chrome-iron ore to peroxide. In carrying out the process they take 200 kg. of chrome-iron ore and about double that quantity of sulphuric acid, which is required for combination with the bases of the ore to form salts. To this is added a quantity of chromic acid in excess of that required to oxidize the protoxide of iron and the mixture is heated to 120° to 150° C. The excess of sulphuric acid is stated to form chromo-sulpho acid ($Cr_2(SO_4)_3 H_2SO_4$) from the sulphate of chromium, and the iron will be precipitated at about 150° C as white sulphate of iron. The two can thus be readily separated by filtration. Instead of using the amount of oxidizing agent necessary for the dissolution of the ore, the inventors propose to use a smaller quantity and to constantly regenerate it by electrolysis. They add to the chrome-iron ore and the sulphuric acid a small quantity of sulphate of chromium or sulphate of lead or other salt capable of being brought to a higher degree of oxidation by electrolysis. This mixture is heated while an electric current is passed through it, and chromic acid is thus produced, which dissolves the chrome iron ore, while it is thereby reduced again. By the electrolysis the oxidation is kept going on until all the ore is dissolved. The process is carried out in a closed vessel, provided with a heating jacket and an agitator, and having electrodes at opposite points, suitably insulated.

*Anode Hook.*—F. W. Cann, Brooklyn, N. Y. Patent 745,479, December 1, 1903. Application filed April 9, 1902.

The inventor constructs his anode hook of two parts, which are connected by threads and a coupling sleeve. The upper part is preferably of copper and bent into the shape of a hook, so as to engage the current conducting rod above the bath. The lower part is threaded into a socket in the top of the anode plate. The lower part is of the same metal as the anode, and when eaten away to a considerable extent is simply replaced, while the upper part is left intact and does not have to be also thrown into the scrap, as is the case when the anode only consists of a single piece.

### Storage Batteries.

*Galvanic Cell.* Lothar Fiedler, London, England. Patent 738,718, September 8, 1903. Application filed December 22, 1902.

The cell described in the specification consists of a rectangular outer containing vessel of a suitable insulating material, which contains a rectangular tube of lead provided with a coating of peroxide on both sides. A negative electrode of zinc, constructed in a peculiar manner, is opposed to the posi-

tive electrode on both sides. Spaces left between the electrodes are filled with an electrolyte of the following composition: 1000 grams of a 24° Bé. solution of sodium silicate, 3000 grams of a 33° Bé. solution of sulphuric acid and 50 grams of mercuric sulphate. After this solution is compounded it is at once poured into the cell, where it solidifies to a jelly. The cell is stated to have an e. m. f. of about 2.5 volts, may be discharged to 1.6 volts and recharged in the same manner as the usual form of secondary cell.

*Galvanic Cell.* Lothar Fiedler, London, England. Patent 738,719, September 8, 1903. Application filed December 22, 1902.

The invention relates to a way of preparing the surface of the zinc electrodes used in the cell described in the preceding specification, and in general in cells of the zinc-lead peroxide type, in order to prevent the zinc from being destroyed by the electrolyte. The process of preparing the zinc electrode is described as follows: A plate of zinc, carbon or other insoluble conducting material is treated as the cathode in a bath of approximately the following composition: Zinc sulphate 1000 grams, mercuric sulphate 50 grams, potassium cyanide 10 grams, made up with water to 30° Bé. The anode may be carbon or zinc; in the latter case zinc sulphate is omitted from the solution. Any other cyanogen containing compound is said to answer the purpose. The action taking place in electrolysis is explained as follows: "The cyanogen set free from the potassium of the potassium cyanide combines with the zinc of the zinc sulphate forming zinc cyanide, CyZn (!), which, combining with the mercury liberated from the mercuric sulphate, forms a "mercuric cyanide of zinc," CyZnHg (!), or "cyanide" zinc amalgam, and a solution containing potassium (!!) and sulphuric acid. The mercuric cyanide of zinc or cyanide zinc amalgam is deposited on the cathode in a firm, even and porous condition." Why the cyanogen liberated at the anode should perform these difficult feats at the cathode, or why the CyZnHg (!) of the inventor should travel bodily to the cathode is a question the inventor does not trouble about. His electrolytic notions appear to be on a par with his chemical ones.

*Composition of Matter for Battery Electrolytes.* W. Peto and W. T. Cadett, Ashlead, England. Patent 735,808, August 11, 1903. Application filed March 14, 1903.

The inventors propose a plastic or semi-solid electrolyte, which is to take the place of the liquid electrolyte at present in use in storage batteries. It consists of powdered or precipitated sulphate of lead moistened with dilute sulphuric acid of about the average strength used in storage batteries. The two are combined in the proportion of about one pound of finely precipitated sulphate of lead to four ounces of dilute sulphuric acid of about 1.2 specific gravity. They are thoroughly mixed until they form a soft plastic mass of a paste-like consistency. The above proportions are stated to be subject to variation, but the requisite proportion of the acid can be easily regulated by allowing the mixture to stand for a while, when the superfluous acid will rise to the top and can be poured off. Sufficient acid ought, however, to be used so as to render the mass soft and plastic, for if it is too stiff, air spaces might be formed by the gassing of the cell, which might impair its efficiency.

*Accumulator.*—W. Kennedy-Laurie Dickson, London, England. Patent 741,675, October 20, 1903. Application filed May 16, 1901.

The cell consists of a containing vessel of hard rubber, glass, etc., lined with a metallic conducting lining from the surface of which thorn-shaped spines project. A layer of active material is firmly pressed to this metallic lining, the thickness of the layer being about equal to the length of the spine. The negative electrodes are made by taking a core of hard rubber, which has numerous perforations, and surrounding it with a hard lead or other metallic sleeve with spines similar to the above. Around this sleeve is placed a layer of paste or other form of material adapted to be formed into active material. After this layer has been applied, the whole electrode is subjected to great pressure, and is afterwards encased in a sack of asbestos. The positive electrode is formed of a solid metallic core resembling in cross-section a maltese cross, surrounded by a layer of active material and compressed into square shape with concave sides, so as to fit in between the round negative electrodes.

*Storage Battery.*—C. W. Kennedy, Rutledge, Pa. Patent 741,044, October 13, 1903. Application filed March 21, 1902.

The cell is composed of a series of bottomless trays of rubber or other non-conducting material. These trays are adapted to receive metallic containing cells, which carry composite plates which form the positive and negative electrodes. The containing cells are made of sheet lead, shaped to form an angular concaved bottom. The convexity of the outer surface of the cell serves to dissipate the gas or air bubbles.

*Electrolytic Apparatus.*—H. B. Ford, New York. Patent 745,588, December 1, 1903. Application filed May 11, 1903.

The principal application of the invention is the construction of secondary batteries. A cell constructed according to the invention is shown in horizontal section in Fig. 4, two positive and two negative elements being shown. Each negative pole element is enclosed in a porous vessel 10, preferably of wood. A conducting plate of copper is enclosed between two zinc plates, all three plates being corrugated vertically, the depth of the corrugations being substantially equal to the internal width of the porous vessel 10. A quantity of mercury is placed into the porous vessel. Assuming the internal dimensions of the cup to be 8 by 5½ inches, and the thickness of the three sheets of zinc and copper to be one-twentieth of an inch, five ounces of mercury will be sufficient. The positive pole electrode is composed of a perforated and corrugated supporting plate 15, which may be of lead with mechanically applied peroxide of lead, or of copper with peroxide of manganese.

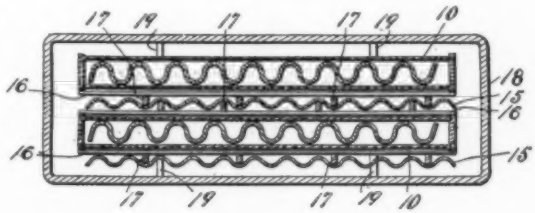



FIG. 4.—STORAGE BATTERY.

Between each positive and negative element is a separating frame, composed of horizontal strips 16, and vertical strips 17, permitting the free circulation of the electrolyte. It is stated that the initial charging current causes the mercury to act upon the zinc and the copper plates in the usual way, and to form, by the absorption of hydrogen, a sponge, containing also some zinc, which sponge expands until the porous cup is practically filled. In the discharge of the battery there is said to be double action of the oxygen upon the zinc and the absorbed hydrogen, the action upon the hydrogen being first completed and resulting in the disappearance of the sponge. As long as the latter remains, the voltage is about 2.5, and upon its disappearance the e. m. f. drops to about 1.5 volts. Dilute sulphuric acid of 25° Be′ may be used as an electrolyte. The five ounces of mercury contained in the porous cup will form upon a full charge a quantity of sponge sufficient to practically fill the cup, the sponge being too soft to adhere to the electrodes, but being retained in contact with them by the walls of the cup. It is stated that if an amalgam hard enough to be retained in grooves or pockets, as proposed before, were used, much hydrogen would be lost.

MISCELLANEOUS.

*Composite Metal Roll.*—C. J. Reed, Philadelphia. Patent 741,413, October 13, 1903. Application filed April 4, 1902.

The rolls described in the specification are intended to be used in the manufacture of paper, and for other operations, where a roll with a hard, smooth and substantially non-corrodible surface is required. The roll is prepared in the following manner: A drum of a base metal, like cast iron, is first coated with a solder, preferably by rotating it in a molten mixture of equal parts of tin and lead. It is then allowed to cool, and is provided with a covering of brass, copper or other non-corrodible material, by closely winding a wire or ribbon of these materials, preferably of rectangular cross-section, upon it, after the wire is first coated with solder. The structure is then heated in order to make the covering closely unite to the drum. The covered drum is then turned true and electroplated with a suitable metal or alloy, like copper, nickel or brass. A tank is shown in the specification, which is filled with a mixture of a liquid electrolyte and a granular non-conducting substance, such as sand, in which the drum is polished and plated simultaneously.

# Correspondence.

## ALUMINIUM AS AN ELECTRICAL CONDUCTOR.

To the Editor of Electrochemical Industry:

Sir—With reference to the comments published on page 547 of your November issue, upon the results obtained in my exposure tests, may I point out that the exposure tests commenced at St. Helen's were abandoned in 1900, and that only the series of exposure tests at Waterloo were carried on for the full period of three years.

There are no chemical works in the neighborhood of Waterloo, and sea air alone can be regarded as the cause of the corrosion of my rods and wires. John B. C. Kershaw.

Waterloo, Liverpool.

## AMERICAN ELECTROCHEMICAL SOCIETY ELECTION.

To the Editor of Electrochemical Industry:

Sir—Nominations for officers of the American Electrochemical Society, to be elected in April, have already been received by the secretary, renominating me as secretary for another year.

I take the earliest opportunity of informing members of the society that it would be impossible for me to serve another year, if elected, and requesting them not to waste their nomination votes on me for that or any other office.

Charles J. Reed.

Philadelphia, Pa.

# Book Reviews.

Das Neue Institut fur Metallhuettenwesen und Electrometallurgie an der Koeniglichen Technischen Hochschule zu Aachen. By Dr. W. Borchers. Halle, a. S.: W. Knapp. Price $2.00

This small book describes the new building devoted to mining and metallurgy, and gives some account in a modest sort of way of the author's labors in his old laboratory. The different furnaces are described with detailed drawings and offer opportunity for many interesting experiments. For instance, who would not like to study the rate of oxidation of copper matte or pig iron in a small converter, so arranged that the percentage of oxygen in gas blown through could be varied from 20 per cent to 100 per cent O.

In reading this book we are struck with the growing complexity of metallurgy. Separations of metals can be made in so many ways, and the metallurgical processes are increasing at an increasing rate. For instance, oil, hydraulic, pneumatic, electrostatic, and electro-magnetic separations can be used on ores, or richer products. Roasting can be done under several conditions. Reverberatory smelting or cupola smelting under oxydizing or reducing conditions can be cited also. Smelting in an electric furnace or electrolyzing at high temperature are other metallurgical means. Then there are the various chemical treatments with solvents, etc., as cyaniding for gold, and electrorefining.

The man who has the ability to use the best of these means for reaching his end, must have a scientific mind to comprehend the scientific facts and must have the ability to discriminate between reactions that work well "in microcosmo" but fail on a large scale, and those which work better in a 50-ton vat than in a beaker. Such is the position of the twentieth century metallurgist.

For those who need hints for a metallurgical laboratory this book would be valuable.

## THE EDISON NICKEL-IRON STORAGE BATTERY.

Mr. Thomas A. Edison's invention of a comparatively very light and extremely durable storage battery, which would be especially suitable for automobile purposes, was first announced by Dr. A. E. Kennelly in a paper read before the American Institute of Electrical Engineers in May 21, 1901. The most interesting point was the announcement that Mr. Edison's new battery meant a radical departure from the lead cell. The new cell was characterized by Dr. Kennelly as an "oxygen lift" cell, for the reason that the chemical action in the cell during charge and discharge consists essentially in a transfer of oxygen from one plate to the other in such a way that the electrolyte—a solution of a caustic alkali—serves only as the "channel" through which the oxygen is lifted, while the one plate is changed to a higher state of oxidation, and the other to a lower state.

At first sight it looks as though a great many varieties of such oxygen-lift cells were possible. As electrolyte, an aqueous solution of potassium hydroxide or of sodium hydroxide might be used, while for the electrodes any metal would be suitable which is easily oxidized, and which, in all states of oxidation, is absolutely insoluble in the electrolyte. This last point—the insolubility of the electrodes in the electrolyte—is really the fundamental technical problem which was to be solved in the invention of an oxygen-lift cell, not on paper, but for practical use.

We may now, for a moment, assume that we have an oxygen-lift cell M. KOH, RO, where M and RO are the two electrodes, and KOH the electrolyte. M and R are assumed to be two metals, which, together with their oxides, MO and RO, are absolutely insoluble in KOH. When the cell discharges, the direction of the current through the electrolyte is from M to RO and the action of the current consists in a traveling of K ions towards the RO plate, and of OH ions towards the M plate, with a resulting reduction of the RO plate, according to the equation

$$RO + 2K + H_2O = R + 2KOH$$

and oxidation of the M plate according to the equation

$$M + 2OH = MO + H_2O.$$

The total electrochemical action in the battery is, therefore, given by the equation (obtained by summation of the last two equations)

$$M + RO = MO + R.$$

The reaction of the oxygen-lift battery is thus simplicity itself, and this is really the foundation of its special advantages.

Mr. Edison, in a very extended and systematic series of experiments, carefully considered what elements would be suitable for M and R, and soon established that the choice is very limited, on account of the requirement that these elements in all states of oxidation must be insoluble in KOH. As well

known, he has finally adopted nickel and iron; during discharge a higher oxide of nickel is reduced to a lower oxide, while the iron is oxidized.

Mr. Edison's claim is that he has been the first to construct an oxygen-lift cell which is really an oxygen-lift cell; that he has been the first to prepare electrodes which are really insoluble and active in the caustic potash solution when used continually in practice.

It is true that before the announcement of the Edison battery, others have had the idea of an oxygen-lift cell. Especially Mr. E. W. Jungner, a Swede, has taken out some patents in this direction, and Mr. T. von Michalowski has patented a method of making nickel oxide electrodes (although he uses a soluble zinc plate as the other electrode, and thus has not an oxygen-lift cell). But these were not the first ones working in this line. The general idea of oxygen-lift cells is still older. In a French patent (233,083, 1893), Darrieus explains quite clearly the general scheme. But what Mr. Edison claims, is that none of those who worked in this direction, before him, ever made a battery which turned out to be in practice what it was claimed on paper; that none of the methods described before him for making the electrodes for such purposes, would yield an active material, really insoluble in the electrolyte. To explain the situation, comparison might be made with the endeavors to design a "carbon cell;" the general scheme of such a cell is well known, and has been taken up by numerous inventors, so that when a carbon cell should really be invented some day in future, many would probably claim priority; yet it is a fact that so far nobody has made a carbon cell which would work in practice.

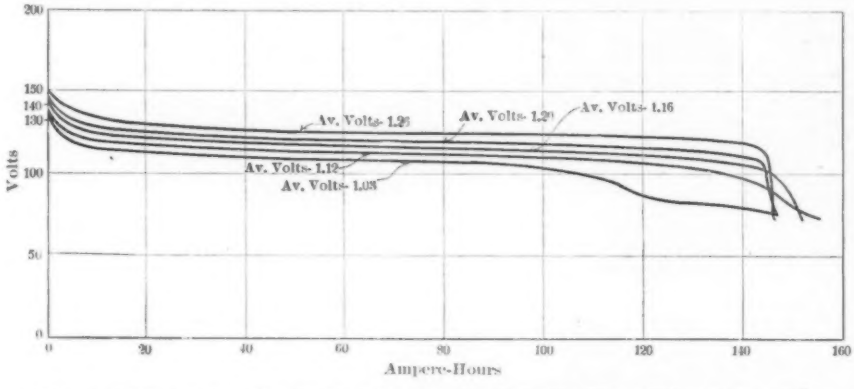



FIG. 1.—TEST OF LATEST TYPE OF EDISON BATTERY FOR DISCHARGE RATES BETWEEN 20 AND 100 AMPERES. WEIGHT OF COMPLETE CELL 12 LBS. 9 OZ.

Since the first announcement of the Edison nickel-iron battery in May, 1901, it has taken more than two years of elaborate and systematic work to bring the battery up to the conditions of chemical and mechanical perfection, in which Mr. Edison wanted to have it, before he would place it on the market. The first type of cell placed on the market is described in detail below, and profusely illustrated. Some very interesting results obtained with this type of cell by Prof. Hospitalier in Paris are also recorded below.

In the meanwhile, however, Mr. Edison has found that he can improve this type of cell, by using twice the amount of active material of nickel as in the former type of cell, while the amount of active material of iron is the same as before. He therefore uses always two nickel plates together, where in his former type of cell only one such plate was used. This improved type of cell will soon be placed on the market. The results of tests of this improved type are given in Fig. 1.

The weight of cell, complete with solution is 12 pounds 9 ounces. The total ampere hours for the various discharge rates change only slightly, while the average voltage is 1.26 for a discharge rate of 20 amperes; 1.20 volts for 40 amperes; 1.16 volts for 60 amperes; 1.12 volts for 80 amperes, and 1.03 volts for 100 amperes. For the 20-ampere rate, the watt hours are 140 ampere hours, multiplied by 1.26 average volts, i. e., 176.4 watt hours, hence 14.0 watt hours per pound of cell complete.

Of theoretical interest is the drop of the voltage curve at the end of discharge at the highest discharge rate (after 100 ampere hours at a discharge rate of 100 amperes). This drop is attributed by Mr. Edison to the concentration changes in the porous plates, which theoretically develop during discharge, the concentration in the pores of the active iron material decreasing, and the concentration in the pores of the active nickel material increasing, while the total concentration remains unchanged (E. F. Roeber, *Electrical World and Engineer*, vol. 37, page 1,105; *Transactions American Electrochemical Society*, vol. 1, page 195). But this drop is small, in agreement with the theory; and it is remarkable that such a drop of voltage is only with the highest discharge rate, and at the end of the run. This shows that the active mass in the Edison cell is of sufficient porosity to allow a quick exchange of electrolyte between the pores of the plates and the outside.

We regret that we cannot give the details of the preparation of the active material. We may simply mention that the greatest care is taken to employ absolutely pure materials, and that extensive special apparatus are used to purify all materials used in the cell.

One of the latest developments which should be of special interest to electrochemists, is that Mr. Edison has succeeded in making the containing iron jars of his battery by simple electrolytic deposition upon a mould. The process is very cheap, but requires some space; a detailed description of the method cannot be given on account of pending patent applications. Mr. Edison states that the task to make a durable and perfect iron jar by electrolytic deposition, seemed at first quite hopeless; "but you can solve all such problems, if you only keep on experimenting." The currogations in the sides of the zinc jar are made afterwards, and the iron jar is then nickel plated by the process described below.

MECHANICAL CONSTRUCTION OF THE EDISON STORAGE BATTERY.

In general appearance the cell combines elegance of design and finish, with a most solid and enduring mechanical construction. The entire cell is constructed of nickel-plated steel, except for a small amount of hard rubber used to insulate the plates from the sides, bottom and cover of the containing envelope and each adjacent plate from its neighbor.

Each individual steel piece employed in the construction of the cell is plated with a coat of nickel, which, by a special process, is fused to the steel. This process of Mr. Edison of plating steel with nickel is quite interesting in itself, and deserves some description. It may be applied to sheets or other forms which are subsequently drawn, stamped or pressed, or to articles which already have their ultimate shape. It is a pretty illustration of the fact that, even in the difficult case of nickel plating, any subsequent danger of pealing off may be avoided if the fundamental principle is taken into consideration that the alloying power of an electrolytic deposit with the coated metal underneath is a factor determining not only the strength with which the deposit adheres, but also the length of time the plated article will wear and resist corrosion (L. Kahlenberg, ELECTROCHEMICAL INDUSTRY, February, 1903, page 201). Mr. Edison plates the pieces of steel first in an ordinary nickel-plating bath, with a coating of nickel. By this method

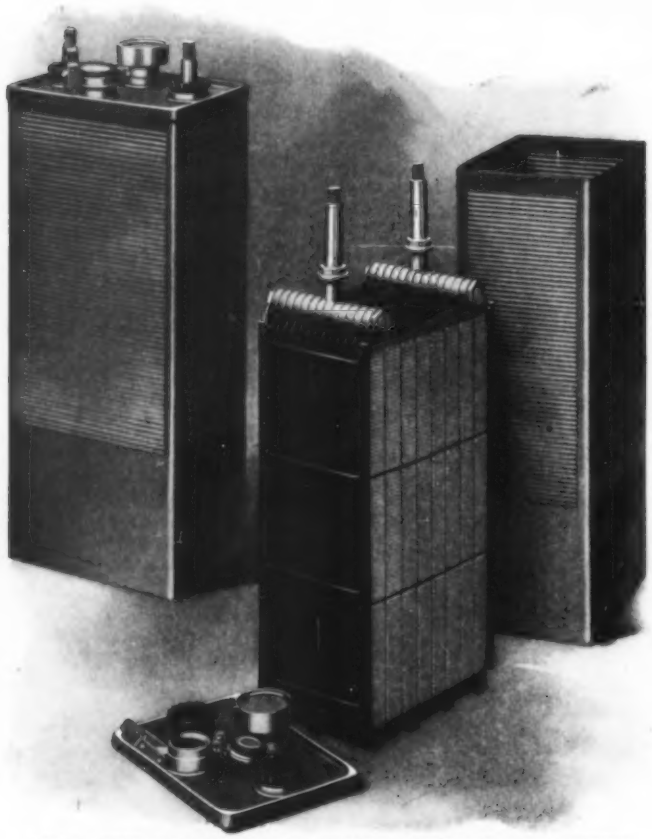


FIG 2.—COMPLETE CELL, CAN, PLATES ASSEMBLED AND COVER

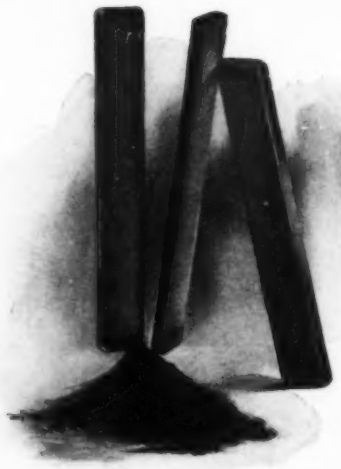


FIG. 3.—TWO PARTS OF POCKET WITH LOOSE MATERIAL, ALSO LOADED POCKET

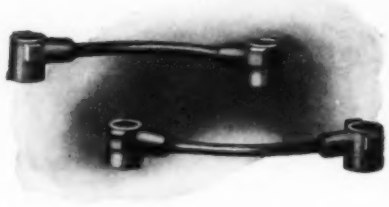


FIG. 4.—CELL CONNECTORS.

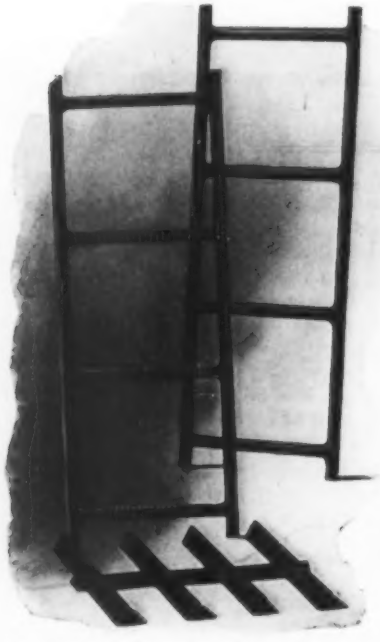


FIG. 5.—HARD RUBBER PLATE SEPARATORS AND CELL INSULATING PLATE.

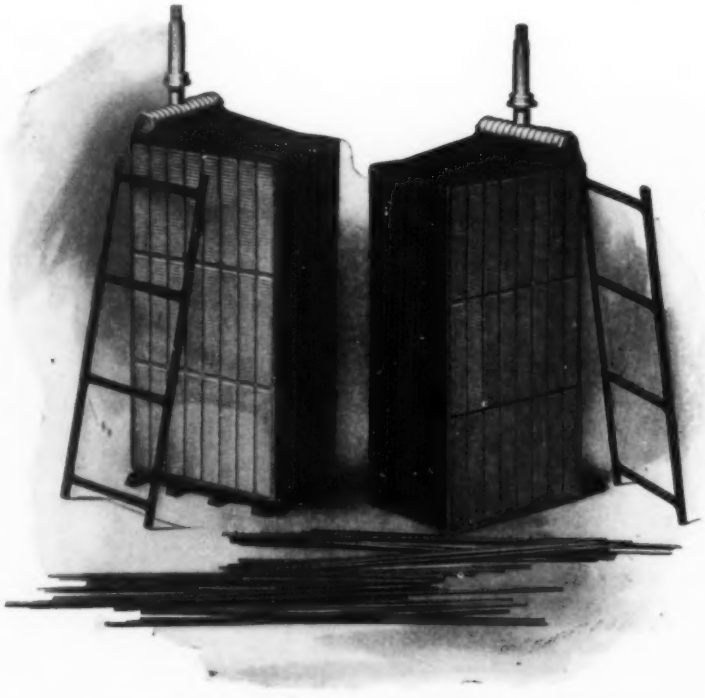


FIG. 6.—GROUP OF NICKEL AND IRON PLATES WITH PLATE AND PIN SEPARATORS

no alloying is produced between the nickel and the iron. Mr. Edison therefore accomplished this end artificially. The pieces are stacked together, and introduced into a cast-iron chamber or clay retort, in which a non-oxidizing atmosphere is produced by the passage of an inert gas, preferably hydrogen. While the current of hydrogen is passing, the nickel-plated steel articles are heated to a bright yellow heat in order to alloy the

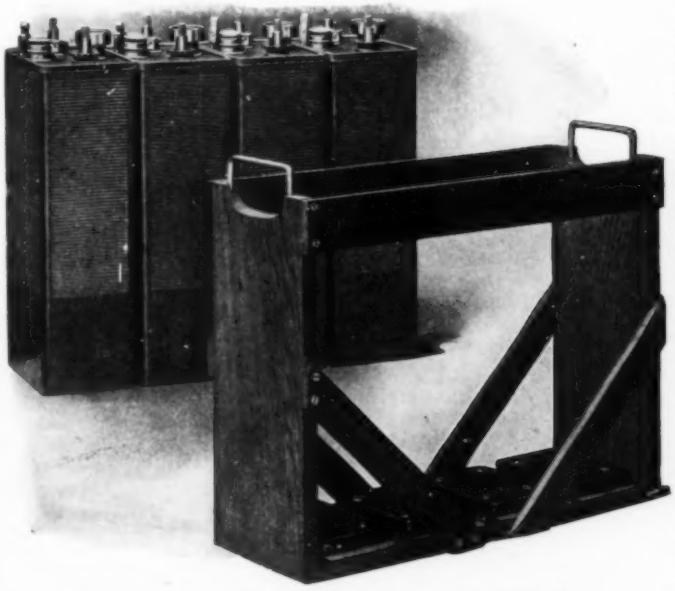


FIG. 7.—TRAY WITH FOUR CELLS IN BACKGROUND.

coat of nickel with the steel backing. The weld thus obtained is so good that the nickel film will not crack or flake off during the subsequent mechanical treatment to which the articles are subjected. The passage of hydrogen gas is continued until the temperature has dropped below the point of oxidation.

The active materials—consisting of specially-prepared oxides of nickel and iron—are held in very finely perforated cups or pockets, each pocket being made in two sections, one engaging within the other. Twenty-four of these pockets are placed in suitable rectangular openings in a thin nickel-plated steel grid, and the whole is subjected to a very strong pressure with the effect that the two sections of each pocket are firmly locked together and at the same time securely fastened in the grid. Each pocket almost becomes an integral part of the supporting grid. To this construction are due the mechanical strength and the lightness of the plate.

The type "D" cell of the Edison Storage Battery Company consists of 28 plates. Fourteen plates with an active material of nickel oxides are strung on to a connecting-rod, to which is fastened a suitable binding-post. Each plate is separated from the next by a spacing washer and the whole is held firmly in place by a nut which screws on the end of the connecting-rod. These 14 nickel plates are connected to the positive pole of the cell. Fourteen plates with an active material of iron oxides are assembled in identically the same manner, and are connected to the negative pole of the cell.

The positive and negative elements are so assembled that each iron plate has a nickel plate on either side of it, and each nickel plate an iron plate on either side of it, except in the case of the two end plates, one of which is a nickel, the other an iron plate. The outer surfaces of these two plates are in juxtaposition with two sheets of hard rubber that insulate the plates from contact with the sides of the containing jar.

The iron and nickel plates are prevented from coming in contact by means of hard rubber rods of a diamond shaped cross-section, a number of which are placed between each set of abutting nickel and iron plate surfaces.

The containing jar is made of corrugated sheet steel, the sides of which are prevented from coming in contact with the plates by the sheets of hard rubber mentioned above. The ends and bottom of the jar are protected from contact with the plates by means of specially designed pieces of hard rubber.

The cover is securely soldered to the jar, and is provided with two stuffing boxes, through which the binding posts extend, and with two other mountings, one, called the "separator," for separating the spray from the gases when the battery is charged, thus preventing loss of potash and causing the gases to be inodorous, the other, called the "filler," for filling in the electrolyte, and from time to time the distilled water.

The "filler" has a water-tight cover, which is held in place by a strong catch. Fastened to the cover is a small spring which causes it to fly open when the catch is released, and it cannot be closed again without some small pressure being exerted, nor will it stay closed unless the catch is securely fastened. This insures that the cover, when in place, shall always be water-tight, and also minimizes the chance of accidentally leaving the cover open, and the possible spilling of solution should the cells be severely agitated.

Each individual cell is held securely in place and free from contact with its neighbor by a little rubber device, which performs the double office of insulator between cells and lock to hold them firmly in position in the trays. Every cell rests upon a thin sheet of hard rubber, pressed into a suitable shape. This effectually insulates the cells from the bottom of the

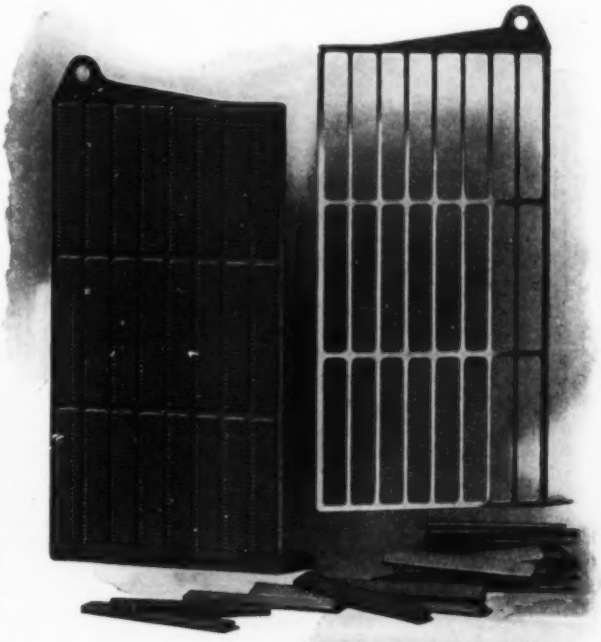


FIG. 8.—GRID AND GROUP OF POCKETS CONTAINING ACTIVE MATERIAL, TOGETHER WITH FINISHED PLATES.

trays. In the bottom of each cell are four small indentations. These fit over conveniently arranged little wooden buttons protruding from the upper side of the tray bottom and prevent the cells from becoming displaced by sudden jolts or shocks, while affording a very rigid yet elastic support.

The connection between cells is made by means of heavy, solid copper wire, well nickel-plated. On the ends of each copper connector are screwed specially shaped steel-lugs, which fit over the binding posts and make a taper joint connection with them, insuring a perfect electrical contact. A nut holds each lug securely in place, so as to make bad contact impossible, even though the battery may be subjected to extremely violent jolting in automobiles.

A socket-wrench for removing the nuts which hold down the connectors, and a specially designed jack for lifting the lugs from the binding posts when disconnecting the cells, are accessories belonging to the outfit of each battery; also a funnel for adding the distilled water, equipped with an indicator which shows when the right amount of solution has been put in the cell.

### Tests of the Edison Storage Battery.

As was already noticed in these columns, the Edison battery has been tested by a number of authorities in the storage battery field. Results of such tests made in England by Mr. W. Hibbert are given in a recent paper of this gentleman, read before the (British) Institution of Electrical Engineers. The main results obtained by Mr. Hibbert were already given in our issue of October, 1903, on page 517. The additional information given in his Institution paper relates mainly to the durability of the battery, about which he speaks very favorably.

Of still greater interest appear to be the results of Prof. E. Hospitalier, the well-known French authority on storage batteries. From a paper published by him in a recent number of *L'Industrie Electrique*, the following information is gathered. The cell tested by Mr. Hospitalier was type 17D, the dimensions of which are as follows:

| | |
|---|---|
| Length in the direction of plates.... | 13 cm. |
| Thickness ..... | 9. cm. |
| Height of jar ..... | 30.2 cm. |
| Height including binding posts ..... | 33.5 cm. |

The weight of the cell was as follows:

| | |
|---|---|
| Electrodes ..... | 5.925 kg. |
| Connections ..... | 0.060 kg. |
| Electrolyte ..... | 1.785 kg. |
| | 7.770 kg. |

Before the test was begun, in accordance with instructions from Mr. Dick, who represents the Edison Storage Battery Co. in Europe, the cell was charged with 30 amperes for 30 hours, and discharged with 30 amperes down to 0.75 volt; it was then charged with 60 amperes for 10 hours and discharged with 30 amperes. After that the real test began.

Prof. Hospitalier made a series of twenty-one charges and discharges, under the conditions given in table I., in the electric laboratory of the Ecole de Physique et de Chimie Industrielles of Paris.

For the charges No. 5 to 17, the rate of charging was only 10 amperes, on account of special conditions. Since a higher rate of charging is more suitable for this special type of battery, the results obtained by Prof. Hospitalier are slightly inferior to those obtained in the tests of Mr. Hibbert, and in the Laboratoire Central d'Electricité, but the differences are too small to affect the mean value, and the results obtained in the different tests may be considered as practically identical, if one takes into consideration that they were obtained under quite different conditions and with different cells.

In table I the letters have the following meaning:

E, electromotive force of the cell in volts before the beginning of the discharge.

$I_d$, constant current of discharge in amperes (discharge No. 12 was made with constant resistance).

U, mean potential difference at terminals of cell during discharge in volts.

T, the length of discharge, in hours and minutes.

Q, total output in ampere hours.

$I_c$, the current of the charge preceding the discharge in amperes (approximate value.)

While a series of twenty discharges is insufficient to enable one to estimate exactly the life and durability of an accumulator, yet, as Prof. Hospitalier points out, these discharges were probably made under conditions which would have put a lead accumulator out of service. Mr. Hospitalier calls special attention to the discharge No. 12, which was made with the cell nearly short-circuited, the initial current being 240 amperes, with 0.95 volt at the terminals. After forty minutes the current had dropped to 180 amperes, with 0.75 volt at the terminals. After this discharge at an excessive rate, the battery was charged with 10 amperes and gave 155 ampere hours in the thirteenth discharge. The fourteenth discharge was made twenty-four days after the charge. Compared with the preceding discharge, it indicates a loss in ampere-hour capacity of 10 per cent, that is less than ½ per cent per day, which is practically insignificant.

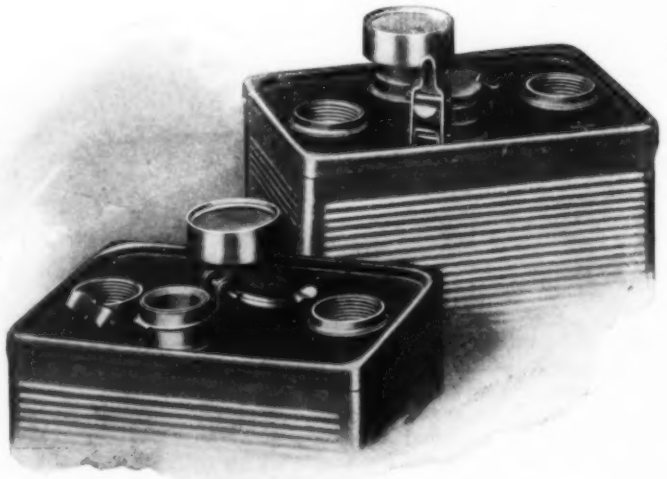


FIG. 9.—FILLER LID OPENED AND CLOSED.

After this discharge the battery was left standing discharged and was recharged on September 4. Discharge No. 15, of September 5, gave again the capacity of the thirteenth discharge, namely, 155 ampere hours.

The influence of a high charge rate is evident from the following discharges. After the seventeenth discharge the battery was short-circuited for seventeen hours, and then charged at a rate of 80 amperes. The eighteenth discharge at a rate of 50 amperes, gave 139 ampere hours, which indicated either an insufficient charge or a temporary loss in capacity. After a new charge the battery gave 154 ampere hours in the nineteenth discharge, and 160 ampere hours in the twentieth discharge, so that the short-circuit after the seventeenth discharge had not destroyed the capacity.

Similar results were obtained in the test of the Laboratoire Central d'Electricité. They show that it is possible to use rates of charging and discharging which would be excessive for the lead accumulator, while the Edison battery does not thereby deteriorate nor lose any appreciable amount of capacity.

A good indication of the life of an accumulator is the total energy furnished by it before it is put out of service divided by its weight. In the extensive competitive accumulator tests of the Automobile Club of France, made in 1899, this figure for the best lead accumulator (Fulmen) was 1.5 kw. hour per kg.

The Edison cell, when tested in the Laboratoire Central d'Electricité, was subjected to 125 discharges, and gave in the average 25 watt hours per kg. in a discharge, that is, in the

whole 3.1 kw. hours per kg., and at the end the capacity was not diminished. This is already more than twice the value of the best lead accumulator in the tests of the French Automobile Club mentioned above, but this does not yet indicate the limit.

Prof. Hospitalier then discusses the disadvantages of the Edison battery. The main disadvantage is that the useful potential difference is about 1.1 volt, while that of the lead accumulator is 1.9. This means that to get the same e. m. f., the number of Edison cells to the number of lead cells is 5 to 3, and in the same proportion the number of connections, etc., must be increased. The closed jar makes examination difficult and repairs expensive, but this inconvenience is compensated by the mechanical strength which renders examination and repairs less necessary. The price is probably higher for the same energy. For the same power, however, the comparison is in favor of the Edison cell if one takes into consideration the high rates which it can stand.

TABLE I.

| Test No. | Date. | E In volts. | $I_d$ In amperes. | U In volts. | T In hours and minutes. | Q In ampere hours. | $I_c$ In amperes. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| 1. | 7 July | 1.52 | 30 | 1.36 | 5 50 | 175 | 60 | Charged July 6th. |
| 2. | 10 " | 1.52 | 50 | 1.38 | 3 30 | 175 | 50 | Charged July 9th. |
| 3. | 13 " | 1.48 | 60 | 1.30 | 2 43 | 163 | 50 | Charged July 12th. |
| 4. | 16 " | 1.48 | 90 | 1.30 | 1 49 | 163.5 | 50 | Charged July 15th. |
| 5. | 17 " | 1.50 | 120 | 1.27 | 1 19 | 158 | 50 | |
| 6. | 20 " | 1.48 | 30 | 1.40 | 5 37 | 168.5 | 10 | Charged with a small motor generator. |
| 7. | 21 " | 1.52 | 50 | 1.41 | 3 18 | 165 | 10 | |
| 8. | 22 " | 1.50 | 90 | 1.40 | 1 46 | 159 | 10 | |
| 9. | 23 " | 1.52 | 120 | 1.30 | 1 17 | 154 | 10 | |
| 10. | 25 " | 1.46 | 30 | 1.36 | 5 07 | 153 | 10 | |
| 11. | 27 " | 1.44 | 30 | 1.34 | 5 15 | 157.5 | 10 | |
| 12. | 28 " | 1.47 | 240-180 | 0.95 | 0 40 | 133 | 10 | Discharge with constant resistance. |
| 13. | 30 " | 1.48 | 30 | 1.38 | 5 10 | 155 | 10 | Charged again on July 31st. |
| 14. | 24 Aug. | 1.34 | 30 | 1.24 | 4 43 | 141.5 | 10 | After 24 days, left at rest after discharge. |
| 15. | 5 Sept. | 1.48 | 30 | 1.35 | 5 10 | 153 | 10 | Charged September 4th. |
| 16. | 9 " | 1.46 | 30 | 1.42 | 5 20 | 160 | 10 | |
| 17. | 6 Oct. | 1.43 | 30 | 1.32 | 5 00 | 150 | 10 | After discharge, short-circuited for 17 hours. |
| 18. | 12 " | 1.45 | 30 | 1.28 | 4 38 | 139 | 80 | |
| 19. | 13 " | 1.52 | 50 | 1.34 | 3 05 | 154 | 80 | |
| 20. | 15 " | 1.46 | 50 | 1.32 | 3 12 | 160 | 80 | |
| 21. | 20 " | 1.44 | 120 | 1.10 | 1 15 | 150 | 10 | |

The watt-hour efficiency varies in the lead accumulator with the rate of charge and discharge. The lower this rate, the higher the efficiency. In the tests of the Automobile Club of France, the mean efficiency for the low rates adopted there was between 70 and 75 per cent. In the tests of the Edison cell in the Laboratoire Central d'Electricité—in which the discharge rate was varied, while the charge rate was maintained at 60 amperes—the efficiency varied between 43 and 57 per cent, that is, 50 per cent in the average. Prof. Hospitalier states, however, that this superiority of the lead cell is only apparent, since, in order to make a fair comparison, it would be necessary to have equal charge and discharge rates, but very rapid charges and discharges would be an impossibility with the lead accumulator.

The two most important characteristic factors of the automobile accumulator besides life and durability are power and energy per unit of weight. The higher these two factors, the better is the accumulator suited for automobile purposes. Mr. Hospitalier's curves, shown in Fig. 10, are very instructive in this respect. I., II. and III. refer to the Edison cell, I. being derived from the tests in the Laboratoire Central d'Electricité, II. from tests of Hibbert, and III. from the tests of Prof. Hospitalier; IV., V. and VI. refer to lead cells; IV. to the Contal accumulator, V. to the Fulmen accumulator, and VI. to the Blot-Fulmen accumulator.

These curves are characteristic and do not require long explanations. They show that for low discharge rates, like 3 or 4 watts per kg. of total weight, the output in watt hours per kg. is about the same for the Edison cell and the Fulmen cell, while that of the Contal cell is slightly higher. But all curves of the lead cell drop rapidly as soon as the discharge rate increases slightly, while the Edison cell curves are distinctly straight lines. For all discharge rates beyond 10 watts per kg. the lead cell is out of question altogether, while the output of the Edison cell decreases only slightly, so that at such a high discharge rate as 25 watts per kg. the energy output is still about 21 watt hours per kg. Prof. Hospitalier points out that this is one of the most valuable properties of the Edison cell,

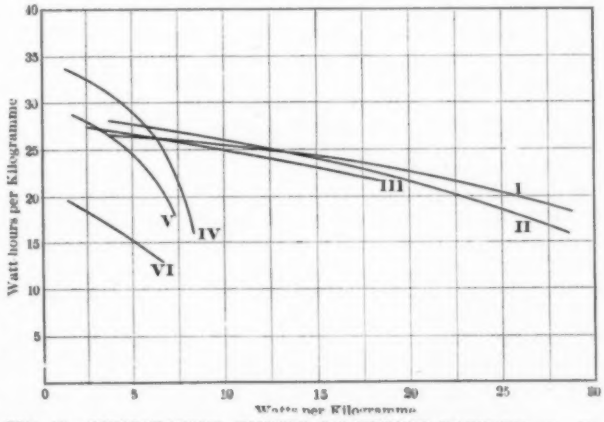



FIG. 10.—COMPARATIVE CURVES OF EDISON BATTERY (I., II., III.) AND LEAD ACCUMULATOR (IV., V., VI.).

and that with respect to this property it maintains a unique position among all storage batteries.

From a table of dimensions the following figures are derived, type X and type Y being two lead batteries of a large French manufacturer:

| | Edison. | Type X. | Type Y. | Contal. |
|---|---|---|---|---|
| $dm^3$ per kw. ..... | 60 | 89.4 | 88.4 | 68.8 |
| $dm^3$ per kw. hour. | 21.5 | 17.8 | 17.8 | 15.7 |
| kg. per kw. ..... | 111 | 200 | 200 | 182 |
| kg. per kw. hour. | 40 | 40 | 50 | 36.4 |

These figures show that the Edison battery requires less space for the same power than the other accumulators, but a slightly larger space for the same energy.

Prof. Hospitalier concludes his article by expressing the opinion that the Edison battery represents an important and undeniable progress in electric automobilism. Its capacity of giving great power per unit of weight will permit to use lighter batteries in carriages which have to make only short trips per day, and thus to diminish the whole weight of the carriage. The possibility of rapid charges will also enable one to make longer trips, since a charge can be made in less than two hours without any deterioration of the battery. Should the discharged battery be left to itself for a few days without being charged again, it will be sufficient to recharge it twice, in order to bring it back to its initial capacity, and no harm will be done.

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## ACID RESISTING BRICKS AND RINGS FOR USE IN PACKING GLOVER AND GAY-LUSSAC TOWERS

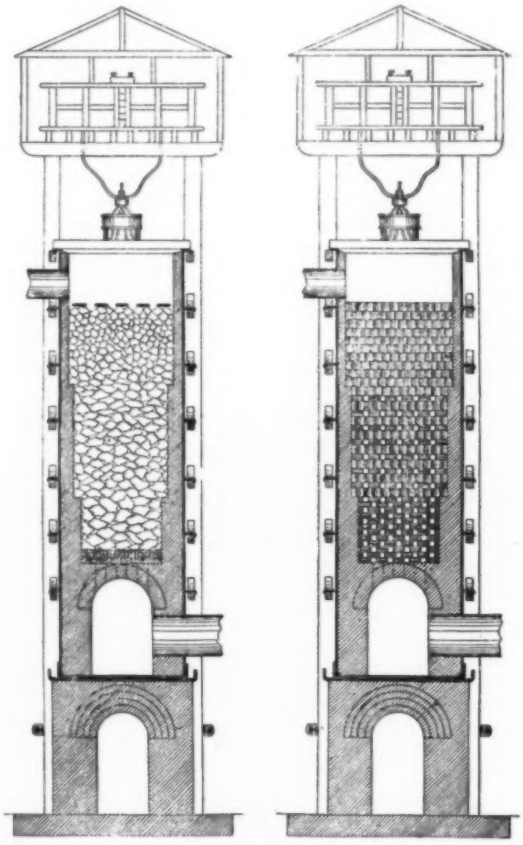
In sulphuric acid factories the Glover and Gay-Lussac towers are well known and highly important accessory apparatus. It was formerly supposed that coke was especially adapted as a packing for these towers on account of its porosity. Prof. G. Lunge, the well-known authority on chemical engineering, has pointed out long ago that this opinion is erroneous. In the first place, porous coke is worthless for a coke tower for which dense coke is indispensable. Secondly, the pores would at once be filled with the liquid, which thus would not come into contact with the gases passing outside. The assumption that coke is not acted upon by the gases or liquids within the tower, has also been proven conclusively to be erroneous. This without doubt accounts for some of the losses in the manufacture of sulphuric acid, when coke is used as a tower packing, and it also explains why the ordinary coke towers must be repacked every year.

In view of these facts, it is not surprising that coke as a tower packing has gradually been replaced by a chemical stoneware packing in form of acid bricks and rings. The accompanying illustrations show side by side a Glover tower with coke packing arranged in the best possible way (at the left side) and one with stoneware packing (at the right side), acid resisting bricks and rings being used in the latter case, as made by Messrs. Richard C. Remmey & Son, of Philadelphia, and the arrangement of these bricks and rings in the illustration shows that there is nothing left to chance. The acid by its downward flow is spread in thin films over the surface of the stoneware. As it drops from one layer to another it strikes on the flat upper surface of the lower layer and is scattered in the form of minute drops in all directions, and taking a new position passes down the succeeding layer in films which expose the greatest possible surface to the action of the ascending gases. The flow of the liquid is constantly interrupted, without in any way impeding the upward current of gases, thus having no pernicious effect upon the draught through the sulphur of pyrites burners.

These bricks and rings are made by Messrs. R. C. Remmey & Son, who control some of the best kinds of clay for this purpose, in sizes 4 to 6 in. in depth. The apertures through eight layers, view from above, show a very intricate lace work, which demonstrates the film-producing action of the method of packing. The upward current of gases is constantly being developed, having a tendency to cause the liquids to form these films upon the stoneware.

These bricks and rings are practically indestructible, and repacking of a tower becomes a very rare operation. Should a lower portion of a Glover tower become disturbed by the dust of fiercely driven fines burners, flushing the tower is an efficient remedy. A coke-packed tower cannot be so easily cleaned in this way.

The two standard sizes of rings made by R. C. Remmey & Son are an inside diameter of 4 and 2 in. respectively, with outside diameters of 6 in. and 4 in., a height of 4 in. and 3 in. and a weight of 72 and 21 ounces respectively. The smaller



GLOVER TOWER WITH COKE PACKING (LEFT HAND), AND STONEWARE PACKING (RIGHT HAND).

and lighter rings are placed nearest the top of the tower, in order to effect a finer sub-division of the descending acid and a greater surface exposure of films.

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Recovery of Gold from Telluride Ores.—On this subject, which was dealt with in Dr. W. H. Walker's Electrochemical Society paper, a recent consular report from Germany gives the following notes: The discovery in recent times of extensive deposits of telluride-gold ores in Western Australia and the United States—notably at Cripple Creek, Col.—has given special importance to this subject, and it has been found on investigation that, so far as can be ascertained, the most improved and effective method known in Germany is one perfected and practiced by the London and Hamburg Gold Recovery Co., which has extensive reduction works at Hamburg, working the telluride-selenic ores from Western Australia. Of the process itself it has only been possible to ascertain that it is partially patented and partially held secret. What is known is that by this process telluride and selenic ores containing gold are pulverized and digested in a solution of cyanide of potash and cyanide of bromium, in proportions of 75 per cent of the former to 25 per cent of the latter. The method of precipitating the gold is kept secret, but it is certain that the process recovers 95 to 96 per cent of the gold contained in the ores, and this proportion is often as high as 97 or even 98 per cent.

## CENTRIFUGAL MACHINE FOR CHEMICAL LABORATORIES AND FACTORIES.

Manufacturers of chemicals and of pharmaceutical preparations as well as research chemists in laboratories have felt for some time the need for an efficient apparatus which would rapidly and easily separate crystals or precipitates from their mother liquors. Such an operation may be accomplished in different ways, like decantation, free filtration, filtration under pressure and separation by centrifugal force. Decantation requires time, and will not yield dry solids. Free filtration is quite suitable as long as the amount of the solids is small; on the other hand, if the crystalline mass is considerable, a great amount of mother liquor or wash water remains in the crystals and the final drying takes much time. Filtration by vacuum under the filter is seldom satisfactory, and requires considerable time.

Filtration under pressure by means of a filter press is certainly an improvement on the precedent methods, yet is not practical in a laboratory. The main defects of this method are that the cakes obtained contain always a large percentage of moisture, and have to be dried; moreover, the crystals do not

CENTRIFUGAL MACHINE.

retain their perfect shape, on account of the grinding and pressure they are subjected to. The filtering cloths also wear rapidly, the cleaning of the filter press is a long and tedious operation. Finally, filter presses are expensive.

With the centrifugal separation these inconveniences are overcome. The separation is rapid, the crystals retain their perfect shape, and are almost dry; and may be completely dried in a very short time, and the emptying and cleaning of the machine is very simple, since the basket is simply lifted out of the machine, emptied of its contents, washed under a faucet, and the machine is ready for another operation.

The adjoining illustration shows the Cyclone Centrifugal Machine, made by Messrs. C. H. CHAVANT & Co., of Jersey City, N. J., which is intended to serve the purposes of the chemist, as well as of the manufacturer. The revolving basket containing the mass to be separated, has a diameter of 10 inches, and is run by direct belt drive. They also make a smaller size for laboratory use, the diameter being 5 inches. The revolving basket is made of a special bronze alloy of great tensile strength, which will resist acids. In a few minutes any amount up to one pound of dry crystals is separated according to the density of the product. The speed, being about 4,000 revolutions per minute, is ample for an almost complete elimination of the liquids. The cylindrical tank collecting the liquors is enamelled in order to resist the acid liquors, and is provided with a spout for the discharge of the mother liquors or filtrate.

## INDUSTRIAL NOTES

The LOOMIS-PETTIBONE GAS MACHINERY Co., manufacturers of gas apparatus and Crossley gas engines, with headquarters at New York City, have recently opened branch offices at Boston, Pittsburg and Chicago.

TRANSFORMER INSULATION.—Bulletin 5,003, of the FORT WAYNE ELECTRIC WORKS, contains a reprint of an illustrated paper by B. A. Wagner on transformer insulation and the use of the vacuum drying and substitution process.

HYDROGEN SULPHIDE.—The CHARLES GRAHAM CHEMICAL POTTERY WORKS, Brooklyn, N. Y., announce that they manufacture C. L. Parson's hydrogen sulphide generators, made from their special grade of chemical stoneware.

STEAM SPECIALTIES.—We have received from the WRIGHT MANUFACTURING Co., of Detroit, Mich., their illustrated catalogue of steam specialties, giving descriptions of improved safety water columns, steam traps, exhaust heads, etc.

ELECTROPLATING AND ELECTROTYPING DYNAMOS.—We have received from Mr. CHARLES J. BOGUE a very neatly illustrated pamphlet on his dynamos for electroplating, electrotyping and general electrolytic work, which were already described in detail on pages 431 and 516 of vol I. of this journal.

WATER PURIFICATION.—The AMERICAN STEEL & WIRE Co. have issued a pamphlet on water purification, with sulphate of iron, for domestic and commercial uses. The information given in the pamphlet is based on tests, made by Messrs. E. E. Irons and J. E. Campbell, at the waterworks of Quincy, Ill. The procedure is as follows: The sulphate of iron is dissolved in a tank of 3,600 gallons of water. Lime is dissolved in 2 tanks of 7,000 gallons each, sufficient water being used to exhaust CaO, and produces a clear solution. The water of the Mississippi River, from which the Quincy water works are supplied, is charged with the requisite quantity of sulphate of iron, while being pumped up from the river, and the lime is injected after the water has passed the pumps. Charged with both solutions, the water passes into the city sedimentation basin, where the solutions quickly draw from the water by precipitation and coagulation the animal, vegetable and foreign matter, leaving only a small percentage to be afterwards extracted by filtration. The quantity of sulphate of iron used at Quincy is about 1½ grains per gallon of water pumped from the river, which is usually extremely turbid, and the same quantity of lime is used. The result is stated to be a perfectly pure and palatable water, and the cost is said not to be higher than that of other means of purifying water. Sulphate of iron is one of the chemical products of the American Steel & Wire Co. The pamphlet gives many details of the process as operated at Quincy.

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## DIGEST OF U. S PATENTS

PRIOR TO JULY, 1902.

*Compiled by Byrnes & Townsend,*
*Patent Lawyers,*
*National Union Building, Washington, D. C.*

373,691. November 22, 1887. Heinrich F. D. Schwahn, Kansas City, Missouri.

Purifies and decomposes fats, such as oil, tallow and butter, by electrolyzing them at 100° C. The solid products settle.

The cell is a vertical, steam-jacketed cylinder carried by hollow trunnions which serve both as the axles of wheels running on a track and as steam pipes. The steam space is sub-divided by a perforated partition. Steam is also injected directly into the cell. One electrode is a vertical coil of wire which surrounds the other electrode, consisting of a rod carrving S-shaped arms.

448,541. March 17, 1891. Thomas Parker and Alfred E. Robinson, Wolverhampton, England.

Produces iodine by electrolyzing an acidified, aqueous

solution of an iodide, as of sodium or potassium, in a diaphragm cell. The anode is of carbon or platinum; the cathode of iron. The cathode compartment preferably contains a caustic alkali solution. The iodine freed at the anode is drained, washed with cold water and dried in a current of warm air.

460,277. September 29, 1891. Joseph B. Gardiner, Nyack, N. Y.

Regenerates the spent products of primary batteries. E. G. Employs a two-fluid battery with an anode of zinc in acidulated water and a cathode of carbon in a dilute solution of chromic acid produced by treating lead chromate with sulphuric acid. The spent battery solutions, either combined or singly, are treated with potassium or calcium carbonate, evaporated and ignited, giving zinc oxide and potassium chromate, which is dissolved out. This chromate is combined with the lead sulphate obtained in the first operation, reproducing the lead chromate.

466,720. January 5, 1892. Stanley C. C. Currie, Philadelphia, Pa.

Produces insoluble chlorides, as of lead, silver and mercury, by employing the desired metal as anode in a neutral electrolyte, preferably a solution of zinc chloride. Sodium chloride may be added to reduce the resistance. The mercury anode is held in a non-conducting cup. The electrolytic chlorine combines with the anode, giving the desired product, and the zinc is deposited on the cathode, which may be of zinc or lead. The zinc may be subsequently removed from the cathode by reversing the current.

501,578. July 18, 1893. Heinrich Pfanne, Rixdorf, near Berlin, Germany.

Produces varnish by electrolyzing an emulsion of purified linseed oil, water and sulphuric acid, for two or three hours. The cell is a cylindrical, closed vessel having a central, vertical shaft, carrying arms with wire-brush stirrers. The electrodes are two vertical, curved, zinc plates, at opposite sides of the stirrer.

511,450. December 26, 1893. Arthur Amos Noyes and Arthur Austin Clement, Boston, Mass.

Produces para-amido-phenol-sulphonic acid by electrolyzing a sulphuric acid solution of nitro-benzol. The anode, of platinum, is placed in a porous cup containing concentrated sulphuric acid. The porous cup and cathode, of iron, are placed in the nitro-benzol solution, preferably one part in four of concentrated sulphuric acid. Sufficient current is employed to heat the electrolyte to 90°-100° C. The electrolysis is continued until nitro-benzol is no longer precipitated on dilution with water. Water is then added to the product and the liquid filtered. The solid is washed with water and dissolved in caustic alkali. The sulphonic acid is precipitated from this solution by neutralizing with hydrochloric acid, washed with water and dried. It may be purified by redissolving in alkali and reprecipitating with acid.

541,597. June 25, 1895. J. D. Darling, Philadelphia, Pa.

Electrolyzes molten sodium or potassium nitrate and conveys the gaseous products to a Glover tower for the production of sulphuric acid. Cathode, a closed, cast-iron vessel, from the cover of which depend cast-iron anode-plates. The gases escape from a pipe having a glass section. When the evolved nitrogen peroxide is no longer seen in the glass tube, the current is switched to another cell. The molten residue in the vessel, mainly sodium monoxide, is run off and dissolved in water to produce caustic, the undecomposed nitrates being separated.

541,598. June 25, 1895. James D. Darling, Philadelphia, Pa.

Converts niter-cake and other acid salts into neutral salts, by placing a solution of the salt in the intermediate compartment of a cell having two transverse diaphragms. The end compartments contain a saturated solution of sodium chloride or other salt having the same base as the acid salt. An electric current is passed from lead anodes in the end compartments to a carbon cathode in the middle compartment and the sodium or other base neutralizes the acid salt.

553,593. January 28, 1896. Marius Otto and Albert Verley, Courbevoie, France.

Produces vanillin by electrolytic oxidation of solution of sodium isoeugenate. The anode and cathode compartments, provided with platinum electrodes, are connected by a relatively narrow tube to prevent mixing of the solutions; the anode compartment contains sodium isoeugenate solution, and the cathode compartment sodium hydrate. As the oxidation proceeds the isoeugenate is converted into vanillate, from which the vanillin may be separated by decomposition with oxalic or sulphuric acid. No data as to current.

572,512. December 8, 1896. Heinrich Albert, Biebrich, Germany.

Produces alkali phosphates in a diaphragm cell, the cathode compartment being filled with phosphoric acid solution, and the anode compartment with sodium chloride. On passage of the current, chlorine is liberated at the carbon anode, and the alkali neutralizes the phosphoric acid in the cathode compartment. In accordance with the quantity of the respective compounds may produce mono-, di-, or tri-basic phosphate in the cathode compartment.

579,317. March 23, 1897. Emile Joseph Constam and Arthur von Hansen, Zürich, Switzerland.

Percarbonates are produced in the anode compartment of a diaphragm cell, by electrolyzing, preferably at a temperature of 16° C., saturated solutions of the alkali carbonates. At this temperature the carbonate yields the ions $MCO_3$ and M, percarbonates of the formula $M_2C_2O_6$ being formed by union of two anions. The compound is an amorphous, bluish white salt, decomposing in water at ordinary temperatures with evolution of oxygen and carbon dioxide. It is therefore a powerful oxidizing and bleaching agent.

602,873. April 26, 1898. Joseph W. Richards and Charles W. Roepper, Bethlehem, Pa.

Insoluble sulphides are produced by the action of a hyposulphite solution on the corresponding metal anodes. As an example of the process sodium hyposulphite in 10 per cent solution is electrolyzed with cadmium electrodes, and yields directly the sulphide of cadmium or "cadmium-yellow." The reaction proceeds best at 75° C., and the color is brighter if 5 per cent of sodium chloride be added to the electrolyte. Refers also to antimony sulphide, which is best produced in a cold solution.

602,872. April 26, 1898. Joseph W. Richards and Charles W. Roepper, Bethlehem, Pa.

The process is substantially as above, save that an alternating current is employed. The special advantage is that the insoluble precipitate and the hydrogen are produced in alternating succession at the electrodes, and the hydrogen facilitates the loosening of the precipitate of metallic sulphide. No data as to frequency, etc.

630,612. August 8, 1899. Max LeBlanc, Frankfort-on-the-Main, and Hermann Reisenegger, Höchst-on-the-Main, Germany.

Method of producing chromic acid solutions and regenerating such solutions after use for oxidation. Chromium sulphate dissolved in suphuric acid is oxidized to chromic acid in the anode compartment of a diaphragm cell, and is then employed for any desired oxidation. If the reduced solution were returned directly to the anode compartment, the gradual increase in concentration of sulphuric acid would disturb the conditions, wherefore the reduced solution is brought first to the cathode compartment, wherein its sulphuric acid content is diminished, then introduced into the anode compartment for regeneration. In this manner the sulphuric acid concentration is maintained constant.